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SYMPOSIUM

ON

THE ELASTICITY OF CRYSTALS

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RADIOACTIVE BERYLLIUM IN THE ATMOSPHERE AND ON THE EARTH

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Abstract

It is estimated that about 1,000 nuclei of radioactive Be^{10} (2·7 million years half-life) are produced per square meter per second by cosmic ray induced nuclear disintegrations in the atmosphere. The conditions for observing the resulting activity in rain water and in various regions on the earth are favourable and may be useful for measuring sedimentation rates and other geological surface changes during the Tertiary.

Long-lived radioactive isotopes are continuously being created in the upper atmosphere as a result of nuclear disintegrations caused by cosmic ray particles. Carbon 14[1] and recently Tritium,[2] have been shown to arise in this manner. Since the atmosphere contains also large amounts of stable carbon nuclei in the form of CO_2 and stable hydrogen nuclei in the form of water vapour, these cosmic ray produced radio isotopes are always highly diluted; the samples collected on the earth have, therefore, a correspondingly low specific activity.

There is one other long-lived radio isotope which can be produced by disintegration of nitrogen and oxygen nuclei, the beryllium isotope $Be.^{10}$ Because of its long half-life (2·7 million years),[3] this isotope may be useful for establishing chronology of geological events in the Tertiary. On first consideration one might think that the expected radioactivity is too weak to measure with existing techniques, not only because the production of Be^{10} is probably still smaller than the already small production of tritium; but primarily because the very much longer half-life makes detection of small quantities more difficult. However, these disadvantages may easily be offset by the fact that Be^{10} in the atmosphere is not contaminated by any stable beryllium nuclei.

Presumably Be^{10} will be oxidized fairly rapidly after creation, and will reach the earth dissolved in rain water; these assumptions suggest themselves from analogy with the behaviour of cosmic ray produced tritium.

Though proof is still lacking, I shall assume for the present that the Be^{10} nuclei will reach the earth in a time short compared to their half-life. The dilution of Be^{10} with the stable isotope Be^{9} will be small even after the nuclei have reached the earth's surface, because beryllium is a rare element in the lithosphere, hydrosphere and biosphere. The average beryllium content of igneous and sedimentary rocks has been estimated as two parts per million[4] and the beryllium content of sea water seems to be so small as to have escaped detection.[4, 5] Therefore, it should be possible to obtain on earth, by chemical separation, samples of Be^{10} with a high specific activity.

It has recently been demonstrated[6] that a freshly poured nuclear emulsion is an extremely sensitive β-ray counter for samples of high specific activity; it is capable of measuring, against ordinary background, disintegration rates of the order of 1 dis./hour, provided that the activity can be concentrated in a volume 10^{-5} c.c. or less. This type of detector would be suitable for Be^{10} which emits electrons with an upper energy limit of 550 KeV. It is this refinement in detection technique which makes it hopeful to attempt the separation of Be.[10] It would be sufficient to have 10^{11} nuclei in solution, and a concentration corresponding to about one part of Be^{10} in 10 million. Such a sample corresponds to the specific activity of 5,000 dis./min., cm.^{3} of solution. With conventional electronic counting techniques the radioactive sample would have to be about 1,000 times as large, but its specific activity could be much lower.

The production rate of Be^{10} can be estimated fairly reliably by the following considerations:—

(*a*) The rate of nuclear disintegrations of nitrogen and oxygen in the atmosphere (star production) at the equator is 0·75 per second in a column extending the full height of the atmosphere and having a cross-section of 1 cm.^{2} It increases with latitude and reaches 3·3 per second at latitudes higher than 60°.*

(*b*) The spalliation reactions in light elements observed in cosmic radiation and in experiments with high energy particle accelerators, permit a reasonably safe estimate of the distribution frequency of various disintegration products. It seems that in most cases the collision between a fast nucleon and a nitrogen or oxygen

* These numbers have been calculated using the known intensity of primary radiation at various latitudes, the existing information on collision cross-sections of energetic protons and neutrons in air and the measured altitude variation of star production in nuclear emulsions.

nucleus does not lead to complete disintegration of the latter into singly or doubly charged particles; in the majority of cases larger aggregates of the nuclear matter belonging to the target nucleus will survive. All stable and long-lived nuclides are represented among these residues[7] and a conservative estimate leads to the prediction that 5% of all collisions should result in the production of Be^{10}.

We may expect on earth a decay rate of Be^{10} equal to its rate of production and, therefore, an average radioactivity of 3 to 6 disintegrations per minute per $cm.^2$ of surface area. The total equilibrium accumulation of Be^{10} on earth will then amount to about 1,000 tons.†

It may be possible to detect the Be^{10} soon after it reaches the earth. If we take 90 cm. as the mean annual precipitation,[4] we expect rain water to contain on the average not less than 16,000 Be^{10} nuclei per c.c. One can apparently extract an adequate sample from rain water by means of an ion-exchange column; we have lately extracted Be^7 from water with a comparable beryllium concentration (30,000 atoms per c.c., in the form of radioactive $Be\,Cl_2$) without any particular difficulty.

Ultimately, however, tracing Be^{10} in the oceans and on land presents the more interesting problem, because one may hope to use it for measuring rates of sedimentation in the oceans and on continents, rates of weathering of rocks and various other types of geological surface changes which have occurred during the past few million years. Although it seems impossible at this stage to predict the life-history of the Be^{10} nuclei after they have reached the earth, it is nevertheless possible to present arguments in favour of their being detectable. The nuclei which reach the sea in the form of rain could either:—

(*a*) Form a soluble or insoluble compound and stay in solution or suspension in the sea water.

(*b*) Sink to the ocean bottom.

(*c*) Get adsorbed in the sedimentary deposits on the continental shelves.

(*d*) Become concentrated in organic matter.

† Here I make the assumption that the intensity of cosmic radiation has not changed appreciably for several half-lives. Its constancy has been proven so far only for the past ~ 30,000 years[8]) but the interpretation of recent measurements on the He^3/He^4 ratio in meteorites[9] make it likely that cosmic radiation of approximately equal intensity has been in existence for times of the order of at least several 100 million years.

Whatever their fate, the presence of Be^{10} in the oceans should be observable and measurable.

The least favourable case from the point of view of concentration is the uniform distribution of Be^{10} throughout the volume of the sea. The estimated equilibrium accumulation of 4×10^{12} atoms/cm.^{2} together with an assumed mean ocean depth of 3,800 meters[4] leads to a concentration in sea water of 10^7 atoms/c.c. and therefore (neglecting losses) 10 litres of sea water represent a sample of adequate size. Here the extraction and purification will be somewhat more difficult than in the case of rain water, but by adding Be^7 as tracer (half-life 53 days) a satisfactory chemical procedure can probably be worked out.

If the Be^{10} should form deposits on the ocean floor where sedimentation rates of the order of 1 cm. in 20,000 years have been measured[10] only 5 c.c. of deposit are needed for a sample of adequate strength.

If Be^{10} instead of sinking to the bottom were adsorbed in the sediments of the continental shelves, the samples would have to be larger because of the higher sedimentation rates, but they would probably not have to exceed 500 gm. since the effect of high sedimentation rates is partly compensated by the concentration of Be^{10} from the large ocean area into the smaller area covered by the shelves. Similar quantities of sample would be required for extracting Be^{10} on land from sedimentary rocks formed in the process of weathering of igneous rocks in regions where the surface layers are removed at the rate of about 1 g./cm.^{2} per 200 years. The recovery of Be^{10} from sedimentary rocks presents, however, some additional difficulty; here we may expect a sample of the required size to be diluted with approximately 1 mg. of stable beryllium. Thus, even if the beryllium has been well purified chemically, the specific activity of the resulting sample will be somewhat lower than what seems at present required for detection by the nuclear emulsion technique.

If Be^{10} activity were found on the land surface, it is possible that its cosmic ray origin will manifest itself by a very appreciable latitude effect; in the oceans on the other hand this effect may have become obscured or entirely obliterated by mixing due to ocean currents. The latitude effect if observable should permit conclusions about the constancy or fluctuations in energy distribution of the primary cosmic radiation during the past several million years.

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ELASTIC PROPERTIES OF SINGLE CRYSTALS AND POLYCRYSTALLINE AGGREGATES

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1. Introduction

The author and his collaborators have been engaged during the past ten years in studying the elastic properties of single crystals, polycrystalline aggregates, metals, rock sections, gels, plastics and so on, from different aspects using various ultrasonic methods. Amongst these, single crystals and artificially prepared polycrystalline aggregates are of importance from a fundamental point of view because of their relative simplicity. Experimental work relating thereto is briefly reviewed in the following pages. Work done in other laboratories is mentioned wherever necessary, but exhaustive references to literature are not included.

All solid bodies are characterised by their ability to carry longitudinal as well as transverse elastic waves. The velocities of propagation of these waves are different in different directions and are determined by the elastic constants of the solid. The number of elastic constants, in the simplest case of an isotropic substance is two. In the most general case of a single crystal belonging to the triclinic system, the number required to describe the elastic properties completely is twenty-one. This number gradually reduces as symmetry is introduced, finally becoming three for crystals of the cubic system. Isotropic substances and substances available as large specimens are the easiest to handle as far as experimental technique is concerned. Extension of the methods applicable to such substances to crystalline media and to small specimens presents difficulties. These difficulties have been successfully overcome and results of importance have been obtained for many single crystals. For understanding certain aspects of solid state physics, it is essential also to know how these elastic properties vary with temperature and special methods have been devised for studying this aspect. Some significant results of such a study are included in this review.

A study of the relations existing between the elastic properties of single crystals and those of polycrystalline aggregates and of the extent to which the latter can be determined from the former, is also of special interest. Extensive information is not available in the literature on this subject presumably due to difficulties in securing suitable polycrystalline specimens

and due to lack of proper experimental techniques. The elastic properties of the aggregates depend on the closeness of packing, size of particles and arrangement of the crystallites composing the aggregate. If they are distributed in a random manner in all possible orientations in space (having no preferred orientation), then the polycrystalline aggregates will be elastically isotropic and exhibit only two elastic constants which are independent of direction. Methods of calculation in such a case, based on the idea that the properties of polycrystalline aggregates are average values of the properties of the free crystals composing the aggregate, have appeared in a recent publication by Boas.[1] On the other hand, an ordered arrangement of the crystallites (preferred orientation) will result in a fibrous structure or something simulating it. Such a structure will be elastically anisotropic. A common example of the latter type is wood and there are several other naturally occurring minerals which merit a detailed study from this aspect. Further complications in dealing with some polycrystalline aggregates will arise due to the existence of foreign substances usually in the form of cementing material binding the various crystallites together. The elastic properties of these substances are very much influenced by the nature, quantity and distribution of this cementing material. Such studies have a bearing on the properties of rocks and other naturally occurring materials. Another factor which one has to take into account when studying the elastic properties of polycrystalline aggregates is the interaction between the crystals. This interaction arises due to the fact that a crystal embedded in a mass of other crystals does not behave in a manner similar to a free crystal. However, this interaction can be neglected under certain conditions.

2. Experimental Methods

Almost all the early methods employed for the study of elastic properties were static ones, consisting of bending and twisting of specimens under investigation. Such static methods obviously limit the field of experimental investigation as they require large and faultless specimens and this is not always possible especially when we want to study single crystals. However, the advent of the piezo-resonator and the consequent development of piezoelectric techniques have resulted in the evolution of a number of dynamic methods. An excellent review of such methods has been given by Hearmon.[2]

Three different and distinct techniques have been employed in the work now being described. They are (*a*) the wedge method,[3] (*b*) the total internal reflection method[4], and (*c*) the composite oscillator method.[5, 6] A brief description of these methods is given below;—

(*a*) *Wedge method.*—It is well known that a plane parallel plate of any piezoelectric crystal when used in an oscillator circuit acts as a generator of monochromatic sound waves. If the plate is shaped into a wedge of gradually varying thickness and the exciting frequency of the oscillator is varied, an appropriate portion of the wedge responds to the electrical frequency and generates an ultrasonic beam of the same frequency. Thus, a piezoelectric wedge acts as a source of ultrasonic waves of continuously varying frequency. The lower limit of the frequency range is determined by the maximum thickness of the wedge and the upper limit by the power of the oscillator, the sensitiveness of the detecting device and the breaking stress of the crystal employed. In all cases, we have used either a Z-cut tourmaline wedge or an X-cut quartz wedge with a frequency range of 1 to 12 Mc/S.

The wedge is placed on the crystal plate of known orientation under investigation with a drop of oil in between for securing good acoustical contact and the two are kept lightly pressed between two brass electrodes thus forming a parallel plate condenser, in parallel with the tuning condenser of a Hartley circuit. The arrangement is then lowered into a rectangular glass cell containing a transparent liquid like carbon tetrachloride such that the lower surface of the crystal plate just touches the liquid. The ultrasonic beam from the wedge passes through the crystal and then enters the liquid. The transmission maxima are detected using the Debye-Sears diffraction effects with the usual optical arrangement. Since the sound beam is best transmitted when the frequency of the wedge corresponds to either the fundamental or an overtone of one of the normal modes of the crystal plate, the Debye-Sears pattern will have a maximum intensity at such points. It has been found in practice that the setting for maximum transmission is very sharp and is capable of being reset to within 1 to 2 per cent. The transmission frequency is then measured with an accurate wavemeter.

Transmission maxima thus recorded have to be sorted out and assigned to their appropriate modes. Among these maxima, the strong ones usually correspond to the thickness longitudinal mode. The weaker maxima correspond to the transverse and quasi-transverse modes. They can be transmitted to the liquid medium only as longitudinal vibrations consequential to some sort of a coupling effect. Hence, the diffraction pattern due to these modes will be of low intensity. This difference in intensity furnishes a rough criterion by which the maxima can be sorted out and associated with their corresponding modes. Each of these frequencies corresponds either to the fundamental or one or the other of the higher harmonics of the crystal plate under investigation. The fundamental frequency can then be

determined from the intervals between successive frequencies showing maxima of same intensity.

Knowing the fundamental frequencies of the crystal plate of known orientation, the velocities are calculated from which the appropriate elastic constants are obtained. The detailed mathematical formulæ and the method of calculating the different elastic constants are omitted here as they have been published from time to time.[7]

This method has been successfully applied to several crystals belonging to different crystal systems from the cubic to the monoclinic. It has been subsequently extended to polycrystalline aggregates of alkali halides[8] by making suitable modifications in the experimental technique. The specimens of polycrystalline aggregates are obtained in the following way: pure and dry substances are finely powdered and passed through a 200-mesh sieve. These powders are compressed in a steel mould between two steel cylinders of 1″ diameter at a pressure of about 60,000 lb./in.^{2} The compressed cakes are then ground to uniform thickness on very fine emery cloth. Thus a uniformity of 1 to 2 in 100 is obtained. An X-ray study of these tabloids has revealed that the micro-crystals composing the polycrystalline aggregate are oriented in a perfectly random manner as a result of such a compression.

The density of each one of the compressed cakes is determined to an accuracy of 1 to 2 per cent. directly by evaluating the volume of the circular tabloid and determining its weight in air. While determining the characteristic frequencies of the tabloids, special care is taken to see that the tabloids do not come into direct contact with the liquid in the cell. Otherwise, the liquid gets into the pores of the specimens and vitiates the experimental results. For this purpose, the conventional design of the crystal holder is slightly modified. The lower annular brass electrode on which the specimen under investigation rests, is now replaced by a cup-like vessel, the central hole of which is covered by a thin aluminium foil. The rest of the experimental set-up is just the same as that used for single crystals. The characteristic frequencies of the compressed specimens are determined in the usual way in the frequency range 2 to 10 Mc/S.

The wedge method just described is simple, elegant and requires only small specimens. This last mentioned advantage has made it possible to determine the elastic constants of diamond[9] for the first time. The method has the additional advantage that inclusions or minute crevices in the crystal do not affect the results appreciably. The method is, on the whole, capable of giving elastic constants accurate to about 5 per cent.

In spite of all the abovementioned advantages, the wedge method has certain limitations of its own. As the specimen under investigation comes into contact with the liquid in the observation cell, the method is not quite suitable for porous substances like wood. Further, extension of the method to high temperatures is rather difficult as the liquid has to be heated along with the specimen. Consequently, the diffraction maxima appear blurred owing to convection currents set up in the liquid thus making it difficult to detect the transmission maxima. The method is also not suited to study substances like granites which highly attenuate the ultrasonic beam. In such cases, it becomes particularly difficult to locate the torsional maxima.

(*b*) *Total internal reflection method.*—In an attempt to overcome the abovementioned difficulties, a different technique based on a principle originally used by Bez-Bardili[10] has been adopted by us. Sound velocities in solids are usually much higher than in liquids, so that when an ultrasonic beam passes from a liquid to a solid, the phenomenon of total internal reflection will occur beyond a critical angle of incidence, as in optics. If this critical angle is determined, the ultrasonic velocity in one medium relative to that in the other can be calculated. In the method of Bez-Bardili, a plate of the material is placed in the path of the ultrasonic beam in a liquid and rotated. The emergent beam is detected by the Debye-Sears diffraction method. More recently, Schneider and Burton[11] employed a second piezoelectric crystal to detect the transmitted beam. In our investigation,[4] the pulse technique of Pellam and Galt[12] is adapted to work on this principle.

A pulsed ultrasonic beam is generated by oscillating one crystal and received by another identical crystal, the intervening space being filled with a liquid. The two crystals are ground flat to the same thickness, their fundamental frequency being 1·15 Mc/S and the third harmonic is used throughout the investigation. The specimen in the form of a rectangular plate is interposed in the path of the ultrasonic beam and rotated, thereby changing the angle of incidence of the beam on the plate. The intensity of the transmitted pulse, as indicated by the pattern on the oscilloscope, changes with variation in the angle of incidence. The transmitted beam first exhibits a sharp dip in intensity at the longitudinal critical angle and completely vanishes a little later at the torsional critical angle. The longitudinal and torsional velocities corresponding to these critical angles are calculated assuming the ultrasonic velocity in the liquid. The error in the determination of the longitudinal velocities will be in the range of half to one per cent. The torsional velocities can be determined even with greater accuracy as the angles involved are much larger.

This method has been successfully employed for a study of the elastic properties of many Indian rocks[4] and certain gels,[13] the results of which do not find a place in the present review. The ease and accuracy with which the longitudinal and torsional velocities can be determined make this method superior to other methods in some respects. It has been mentioned that the torsional velocities in certain inhomogeneous rocks like granites could not be determined by the wedge method due to the high attenuation of the sound beam. In such cases, the total internal reflection method is found to be quite successful. However, the method has the disadvantage that it requires comparatively larger specimens and cannot readily be applied to crystalline media. Furthermore, the original difficulty of the specimen coming into contact with the liquid is not eliminated. As such it is not quite suitable for high temperature work.

(*c*) *Composite Oscillator method.*—The composite oscillator method originally developed by Balamuth[5] and Rose[6] is free from the abovementioned difficulties. As such, this method has been set up and adapted by us for a study of crystal elasticity. In this method, a suitably cut quartz rod is cemented to the crystal specimen end to end, both of them having the same cross-section. The quartz rod is provided with silver electrodes to which an alternating potential of constant amplitude is applied. The piezoelectric effect in the quartz rod sets up the required vibrations in the composite oscillator. The resonant frequency is found by observing the variation with frequency of the electrical impedance between the electrodes. The elastic constant of the specimen can then be found from the resonant frequency, the dimensions of the crystal specimen, and certain constants of the quartz rod. For longitudinal vibration, X-cut quartz bars of square cross-section are convenient while torsional vibrations are excited by a Y-cut quartz rod of circular cross-section with four electrodes. It is essential that each specimen under investigation is tried with different quartz rods, until a composite cylinder, whose frequency falls within 5 per cent. of the frequency of the quartz and the specimen, separately, is found. The composite oscillator can conveniently be placed at the centre of an electric furnace and high temperature measurements made with the least difficulty.

This method has been successfully applied to single crystals and polycrystalline aggregates in the author's laboratory both at room temperature and at higher temperatures. Young's modulus Y and rigidity modulus n along (100) direction are directly obtained in this method by the use of cylinders whose length lies along (100). The elastic modulus s_{11} is simply the reciprocal of $Y_{(100)}$ while s_{44} is the reciprocal of $n_{(100)}$. The range of frequencies employed in this method is 90 to 230 Kc/S. The elastic moduli

s_{11} and s_{44} can be determined to an accuracy of one per cent. while the uncertainty in s_{12} varies from 2 to 3 per cent. over the temperature range.

3. RESULTS AT ROOM TEMPERATURE

(*a*) *Cubic crystals.*—Table I gives the elastic constants of cubic crystals determined by employing one or the other of the techniques described in Section 2. Only those values which we consider as final are given. All the *c*'s in this and subsequent tables are in units of 10^{11} dynes/cm.^{2}

TABLE I

Elastic constants of cubic crystals

No.	Substance	c_{11}	c_{12}	c_{44}
1	Sodium chloride	4·97	1·27	1·27
2	Sodium bromide	3·87	0·97	0·97
3	Lithium fluoride	11·9	5·38	5·34
4	Ammonium chloride	3·90	0·72	0·68
5	Ammonium bromide	2·96	0·59	0·53
6	Sodium chlorate	5·09	1·55	1·18
7	Sodium bromate	5·45	1·91	1·50
8	Lead nitrate	4·56	3·09	1·37
9	Barium nitrate	6·02	1·86	1·21
10	Strontium nitrate	4·73	2·18	1·46
11	Ammonium alum	2·50	1·06	0·80
12	Potassium alum	2·56	1·07	0·86
13	Chromium alum	2·37	0·93	0·77
14	Thallium alum	2·9	1·3	0·87
15	Iron pyrites	36·2	−4·64	10·52
16	Zinc blende	10·79	7·22	4·12
17	Galena	12·70	2·98	2·48
18	Diamond	95·0	39·0	43·0
19	Fluorite	16·44	5·02	3·47
20	Magnetite	27·3	10·6	9·71
21	Magnesium oxide	28·6	8·70	14·80

All the alkali halides including lithium fluoride, being ionic cubic crystals, satisfy Cauchy's relation $c_{12}= c_{44}$. The elastic constants of sodium bromide differ from those of Bridgman[14] whose values are given in Table II. r_0 is the interionic distance in Ångstroms as given by Slater.[15]

TABLE II

Elastic constants of alkali halides

Substance	r_0	c_{11}	c_{12}	c_{44}
Lithium fluoride	2·01	11·9	5·38	5·34
Sodium chloride	2·81	4·97	1·27	1·27
Sodium bromide[14] ..	2·98	3·26	1·31	1·33
Sodium bromide	2·98	3·87	0·97	0·97
Potassium chloride[14] ..	3·14	3·69	0·81	0·79
Potassium bromide[14] ..	3·29	3·33	0·58	0·62
Potassium iodide[14] ..	3·53	2·67	0·43	0·42

The ions of the alkali halides all have completed outer shells of electrons of the rare gas configuration and as such there should be some sort of a regularity in their elastic properties.[16] As the interionic distance increases, the elastic resistance of the crystal decreases, that is, the elastic constant decreases. This fact is borne out by all the alkali halides excepting Bridgman's values for sodium bromide. However, with the values obtained in this laboratory in the place of Bridgman's values, the alkali halides show a regular gradation. Furthermore, these values are in better agreement with the theoretical values of Krishnan and Roy[17] ($c_{11}= 4·3$; $c_{12}= 1·0$ and $c_{44}= 1·0$). Also, sodium bromide and galena figure as exceptions in a paper by Kathleen Lonsdale[18] dealing with the vibration amplitudes of atoms in cubic crystals. For the rocksalt type of compounds it is observed that the largest amplitudes for pure longitudinal waves are associated with the cube diagonal which is also the direction of the largest atomic separation. This condition is satisfied by all NaCl type compounds except NaBr and PbS. However, the values obtained in this laboratory for both NaBr and PbS give largest amplitudes along the cube diagonal showing that these two substances do not behave in an exceptional manner. A similar conclusion is reached by a consideration of the amplitudes for transverse waves also.

The elastic constants of diamond[9] are of special interest and have been the subject-matter of much subsequent discussion. Voigt reported a negative value for c_{12} (negative Poisson's ratio) in the case of sodium chlorate and iron pyrites. Mason's[19] finding that this constant is positive for sodium

chlorate has been confirmed by us while the Poisson's ratio for iron pyrites is found to be negative. Two series of isomorphous substances have been studied, the nitrates of lead, barium and strontium and some alums. No definite conclusions are possible unless a larger number of isomorphous substances is studied. Although magnesium oxide is an ionic cubic crystal, it still remains as an extreme example for the breakdown of Cauchy's relation (c_{44} is nearly twice c_{12}).

The elastic constants of mixed alums (Table III) show a regular gradation as the percentage composition of one of the components is varied. It can be seen that the bulk modulus K equal to $(c_{11} + 2c_{12})/3$ decreases as the density increases.

TABLE III

Elastic constants of mixed alums

Substance	Percentage in gm. of Pot. alum	Density	c_{11}	c_{12}	c_{44}	K
Potassium alum ..	100	1·760	2·56	1·07	0·86	1·567
Mixed alum ..	86·5	1·772	2·52	1·05	0·81	1·540
Do. ..	60	1·796	2·47	1·01	0·78	1·497
Do. ..	54·5	1·802	2·44	1·00	0·78	1·480
Chromium alum ..	0	1·845	2·37	0·93	0·77	1·410

Another type of mixed crystals studied is a set of naturally occurring garnets. Seven different specimens of garnets obtained from different sources in India have been studied and the results are given in Table IV.

It is seen from Table IV that the individual constants do not vary regularly with composition, but the bulk modulus varies more or less linearly with the ferrous content, which in almost all the cases happens to be the total iron content.

(*b*) *Other crystals.*—The elastic constants of crystals other than cubic are given in Tables V, VI and VII.

Dealing with physical properties and atomic arrangements in crystals, Wooster[20] has written a section on elastic properties and atomic arrangements in crystals. He has drawn up a table consisting of c_{11} and the hardness of

TABLE IV

Elastic constants of garnets

No.	Density	Ferrous iron (in percentage)	c_{11}	c_{12}	c_{44}	K
1	3·759	21·8	19·7	9·0	5·7	12·6
2	3·673	22·7	19·2	9·9	5·9	13·0
3	3·630	23·6	21·0	10·3	6·7	13·9
4	3·670	23·0	22·2	10·4	7·0	14·3
5	3·750	26·2	22·6	12·6	6·2	16·0
6	4·130	28·7	27·3	15·7	6·8	19·6
7	4·320	33·5	32·7	12·4	8·9	19·2

TABLE V

Elastic constants of hexagonal and trigonal crystals

No.	Substance	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	c_{14}
1	Calcite	13·74	8·01	3·42	4·40	4·50	−2·03
2	Sodium nitrate ..	8·67	3·74	2·13	1·63	1·60	0·82
3	Apatite	16·67	13·96	6·63	1·31	6·55	..
4	Quartz	8·69	10·68	5·76	0·69	1·56	1·74
5	Beryl (Spotted green)	27·81	24·8	6·61	10·01	6·77	..
6	Beryl (Sea green) ..	29·71	26·50	7·54	10·26	7·39	..
7	Alumina	46·6	50·6	23·5	12·7	11·7	9·4
8	Tourmaline (1) ..	26·3	15·1	5·95	6·1	4·9	−0·9
9	Tourmaline (2) ..	30·4	17·6	6·5	8·8	3·5	−0·4

TABLE VI

Elastic constants of orthorhombic crystals

No.	Substance	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{13}	c_{23}
1	Sodium tartrate	4·61	5·47	6·65	1·24	0·31	0·98	3·34	3·52	3·50
2	Rochelle salt ..	4·06	5·20	6·40	1·22	0·30	0·95	2·61	3·27	3·05
3	$MgSO_4 \cdot 7H_2O$	6·98	5·29	8·22	1·07	2·33	2·22	3·90	2·82	2·83
4	$ZnSO_4 \cdot 7H_2O$	4·00	3·22	5·45	0·50	1·70	1·81	1·32	1·08	1·19
5	Sulphur ..	2·40	2·05	4·83	0·43	0·87	0·76	1·33	1·71	1·59
6	Barytes ..	8·62	9·17	10·84	1·20	2·87	2·74	5·23	3·41	3·56
7	Celestite ..	10·44	10·61	12·86	1·35	2·79	2·66	7·73	6·05	6·19

TABLE VII

Elastic constants of a monoclinic crystal (Sodium Thiosulphate)

$c_{11}=4·57$	$c_{44}=0·60$	$c_{12}=1·84$	$c_{16}=-0·69$
$c_{22}=3·31$	$c_{55}=0·57$	$c_{13}=1·68$	$c_{26}=\ 0·25$
$c_{33}=3·02$	$c_{66}=1·11$	$c_{23}=1·83$	$c_{36}=\ 1·04$
		$c_{45}=-0·27$	

the corresponding crystal in order to obtain a rough idea of its variation. The crystals are arranged in the order of decreasing elastic constant and it is found that there is a rough correspondence between c_{11} of a crystal and its hardness. We can say that this general correspondence is true for all the crystals given in the above tables. He further goes on to explain that the value of c_{11} is determined by the tightness of the bonding between neighbouring atoms and the rate of variation with position of the atoms of the forces of attraction and repulsion between them. On the basis of this, he has given a qualitative interpretation for the magnitude of c_{11} for typical crystals like diamond, sulphur, iron pyrites and so on. Further, from a survey of the elastic properties another generalization he made is that where the atomic binding parallel to an axial direction is strong, the corresponding elastic constant is large. He has given a satisfactory explanation of the

relative magnitudes of c_{11} and c_{33} in terms of the structure of the crystals. It is obvious that while such qualitative observations are significant in their own way, there is much room here for quantitative theoretical work.

(*c*) *Polycrystalline aggregates.*—Table VIII shows the elastic constants of some artificially prepared polycrystalline aggregates.

TABLE VIII

Elastic constants of polycrystalline aggregates

No.	Substance	$\rho_{crystal}$	$\rho_{tabloid}$	(c'_{11})		(c'_{44})	
				Mean	Av. calc.	Mean	Av. calc.
1	Potassium chloride	1·984	1·96	3·08	3·18	1·03	1·05
2	Sodium chloride ..	2·168	2·12	4·42	4·51	1·47	1·50
3	Ammonium chloride	1·527	1·50	3·09	3·17	1·01	1·04
4	Potassium bromide ..	2·756	2·67	2·43	2·73	0·81	0·92
5	Potassium iodide ..	3·127	2·95	1·64	2·11	0·57	0·70

In the case of the first three substances whose densities ($\rho_{tabloid}$) lie within about 2 per cent. of the crystal density ($\rho_{crystal}$), the measured average values of c'_{11} and c'_{44} are also lower than those calculated from single crystal constants by only about 2 to 3 per cent. In such cases, we may extrapolate the density and obtain the ideal elastic constant if required. On the other hand, in the case of potassium bromide and iodide where the densities are lower than the crystal densities by more than 3 per cent., the deviations in the average values of the elastic constants are disproportionately larger. In other words, the compressibility of a pressed specimen increases rapidly and out of proportion to the decrease in density, if we depart appreciably from the ideal densities. These results are in general agreement with those of Bridgman[21] and others.

4. TEMPERATURE VARIATION OF ELASTIC MODULI

(*a*) *Single crystals.*—The composite oscillator method already described has been extensively employed in recent years by the author and his co-workers for studying the temperature variation of elastic moduli of single crystals. Nearly a dozen substances including some alkali halides have been

studied so far but only a few typical cases are being cited here. Full details will be published separately. The values of s's are given in units of 10^{-13} cm.^{2}/dyne in all the tables. Sodium chloride, chosen as the test case, has been experimented upon first and the values obtained are in good agreement with those of Hunter and Siegel.[22]

Experimental results obtained with alkali halides reveal the following points regarding their thermal behaviour.

(1) The variation of s_{11} with temperature is greater than that of s_{44} in the alkali halides of the NaCl type.

(2) Contrary is the case with ammonium chloride as the change in s_{44} is greater than that in s_{11} in this case. Ammonium chloride has a structure which is of the CsCl type.

(3) s_{12} decreases with increasing temperature in the NaCl type halides. It increases with temperature in the case of ammonium chloride.

(4) Elastic constants c_{11}, c_{12} and c_{44} all decrease with increasing temperature in all the cases.

Tables IX, X and XI give the results in the three specially interesting cases of iron pyrites, magnetite and sodium chlorate respectively.

TABLE IX

Iron pyrites

Temp. ° C.	s_{11}	$+s_{12}$	s_{44}
28	2·623	0·20	9·361
50	2·632	0·22	9·406
80	2·642	0·25	9·475
100	2·651	0·25	9·517
125	2·662	0·26	9·581
150	2·674	0·28	9·627
180	2·688	0·29	9·674
200	2·696	0·30	9·745
250	2·720	0·32	9·835
270	2·730	0·34	9·890
300	2·743	0·35	9·950

TABLE X

Magnetite

Units = 10^{11} dynes/cm.^{2}

Temp. ° C.	Y_{100}	n_{100}
30	14·41	9·08
90	14·06	9·10
100	14·01	9·11
145	13·82	9·12
170	13·74	9·13
190	13·66	9·15
210	13·59	9·15
255	13·46	9·16

TABLE XI

Sodium chlorate

Temp. ° C.	s_{11}	$-s_{12}$	s_{44}
30	23·50	5·20	84·8
40	23·81	5·20	85·6
60	24·39	5·25	87·0
100	25·65	5·30	90·0
130	26·65	5·85	92·4
150	27·31	5·95	94·2
170	28·53	6·40	96·5
200	29·50	6·50	100·7
210	29·97	6·70	102·3
230	30·98	6·80	106·5
240	32·85	7·10	108·6
250	33·40	7·20	111·2

Iron pyrites is unique in exhibiting a negative Poisson's ratio (positive s_{12}; see Table IX). The positive sign for s_{12} persists throughout the temperature range studied. s_{11} and s_{44} vary linearly with temperature (see Fig. 1) while s_{12} increases slightly. Rate of variation of the shear modulus s_{44} is larger than that of the bending modulus s_{11}.

Elastic constants of magnetite vary with temperature in an unusual manner (Table X). Usually elastic constants of crystals decrease with increasing temperature, provided there is no change of state. As can be seen from Fig. 2, Young's modulus along (100) direction decreases with temperature as usual, while the rigidity in the same direction increases. The

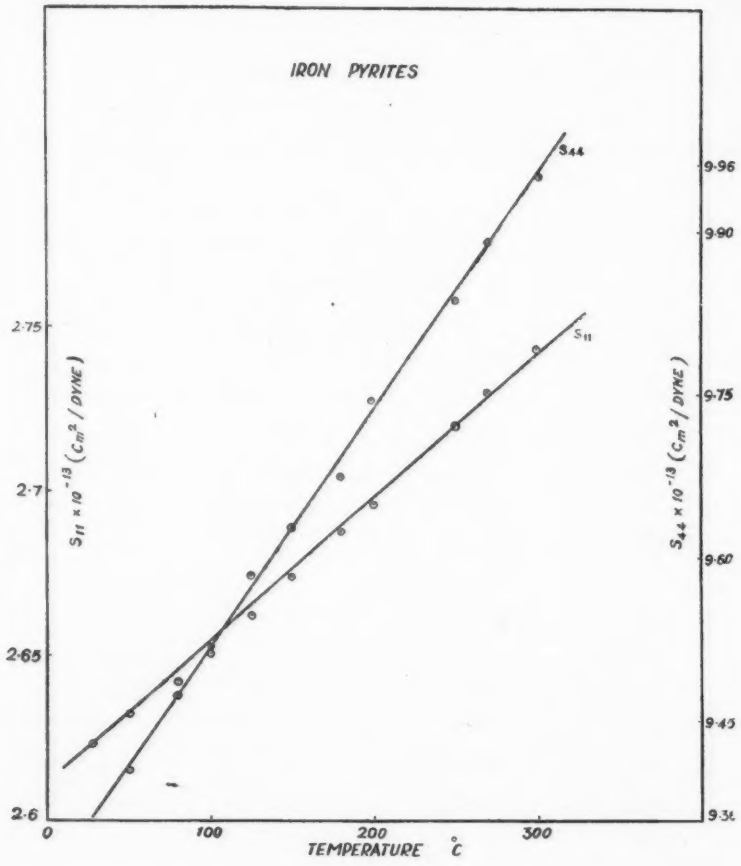

FIG. 1

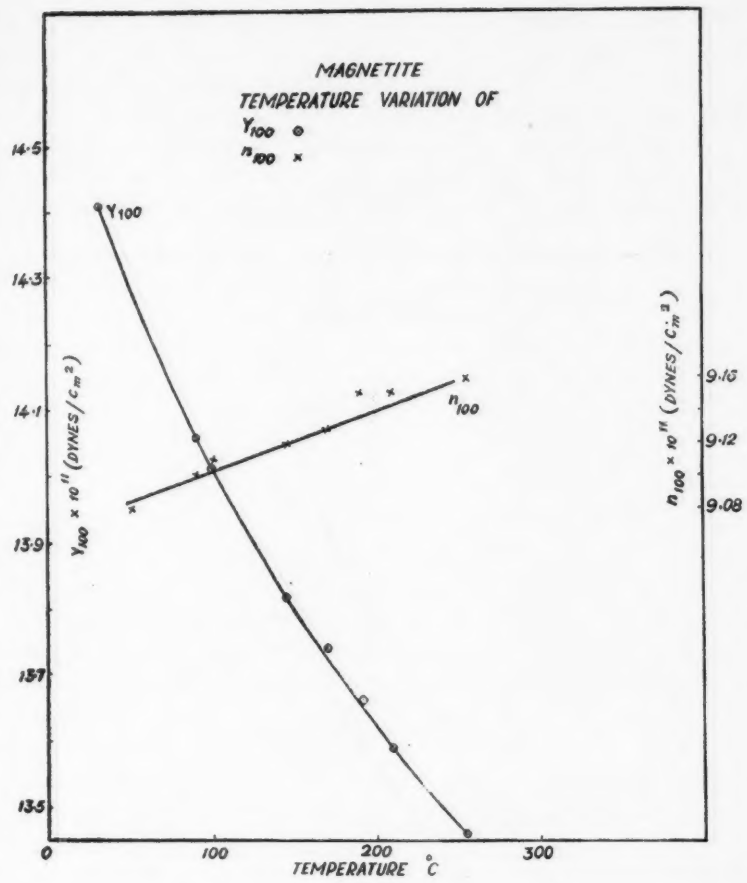

FIG. 2

increase is definite, though small. It has also been found that along (111) direction the behaviour is exactly the reverse. Rigidity decreases with temperature while the Young's modulus increases.* Such an abnormal behaviour may be expected if the crystal undergoes some transition in the particular temperature range, but the region under study is far removed from its Curie point and the low temperature transition as well. Hence the results obtained are indeed likely to be of special significance.

* Detailed results are not reproduced here.

A systematic study of the elastic properties of crystals in the vicinity of their melting points is bound to throw light on the mechanism of melting. The fact that sodium chlorate has no water of crystallisation together with the fact of its having a comparatively low melting point prompted a study of its elastic behaviour upto 250° C. (see Table XI). s_{11} varies linearly with temperature upto 200° C., above which it varies rapidly and non-linearly (Fig. 3). The effect is more pronounced in the case of shear modulus, s_{44}, as one should expect it to

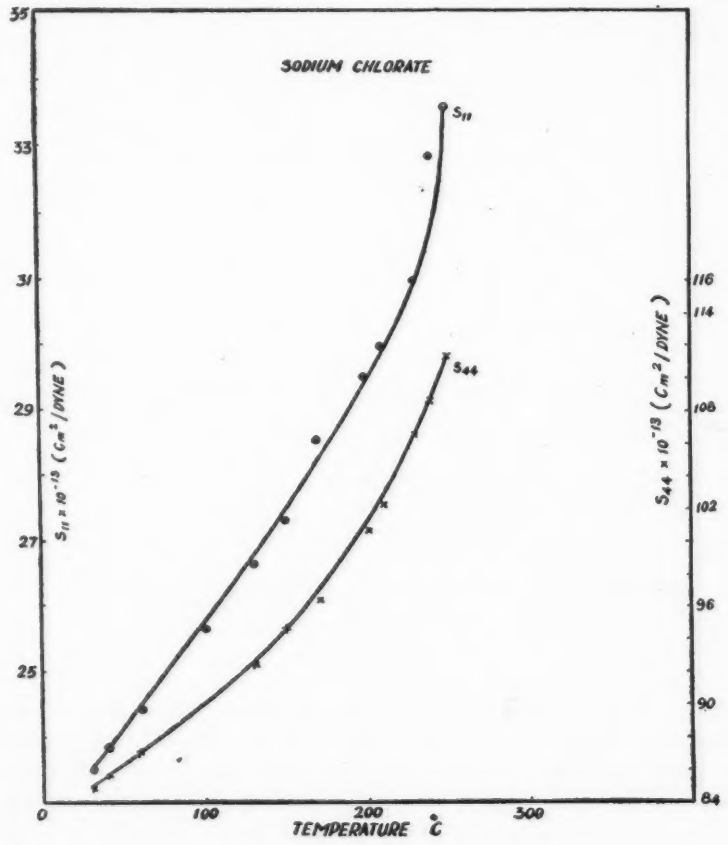

FIG. 3

be. These results afford confirmation of similar results reported earlier by Mason.[19]

(*b*) *Polycrystalline aggregates.*—The elastic properties of polycrystalline aggregates of a few alkali halides, namely, sodium chloride, potassium chloride, potassium bromide and ammonium chloride have also been studied at high temperatures. Results in one typical case are presented in Table XII.

TABLE XII

Polycrystalline sodium chloride

Temp. ° C.	$(c'_{11})_{Av}$	
	Measured	Calculated
27	4·42	4·42
100	4·31	4·26
200	4·06	4·01
292	3·74	3·73

The measured values of $(c'_{11})_{Ae}$ compare well with those calculated from single crystal constants at different temperatures. In fact, in all the four cases studied, the thermal behaviour of the aggregate is in complete agreement with that calculated from the single crystal constants at different temperatures.

5. GENERAL REMARKS

From the standpoint of solid state physics with particular reference to the nature of interatomic and interionic forces in crystals, experimental studies of the elastic properties of single crystals do possess a great significance. Hitherto, though it has been possible to obtain data for quite a large number of single crystals at the room temperature, we have not had extensive work on their temperature variation reported in the literature. Methods developed and described in this article have enabled us to extend the investigations on elasticity into the region of higher temperatures and obtain useful and interesting results. Application of these methods to polycrystalline aggregates is expected to lead to a thorough understanding of the elastic behaviour of the rocks and the crust that constitute the earth at different depths thus possessing different temperatures. It is earnestly hoped that the data presented here as well as the results of the work that is still under progress will ultimately help in the construction of a full and coherent picture of the crystalline forces as well.

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ELASTIC CONSTANTS OF CRYSTALS FROM LIGHT SCATTERING MEASUREMENTS*

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1. Introduction

According to the theory of Einstein which was later elaborated by Leon Brillouin, the scattering of light in a material medium is ascribed to the coherent reflection of light waves by the periodic stratifications produced by the elastic (sound) waves of thermal origin assumed to be present and traversing the medium in all directions. One of the important consequences of Brillouin's theory (1922) is that the moving elastic waves would give rise to spectral shifts of frequency in the diffused light which are in the nature of a Doppler effect. The simple equation derived by Brillouin for the change of frequency is the following:—

$$\frac{\Delta\nu}{\nu} = \pm \frac{2v_e}{c} n \sin \frac{\theta}{2} \tag{1}$$

where

$\Delta\nu$ = is the frequency shift of the scattered light.

ν = the frequency of the incident light wave.

v_e = velocity of the elastic waves giving rise to scattering.

c = velocity of light.

n = refractive index of the medium.

θ = angle of scattering.

Several investigators have considered the theory of the thermal scattering of light in crystals as proposed by Brillouin and came to the conclusion that in a crystal only three pairs of Doppler components occur in the scattered light due respectively to the three types of elastic waves which are propagated with different velocities in any given direction in the crystal. The symmetry of the crystal was not taken into consideration and the influence of birefringence on the Brillouin components was neglected. However, Chandrasekharan (1950, 1951) has shown recently that the birefringence of the crystal when taken into account leads to the remarkable result that there are in general not three but twelve Doppler components which can appear

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in the case of a birefringent crystal. The most general expression for the birefringence of the crystal is given by

$$\frac{\Delta\nu}{\nu} = \pm \frac{v_e}{c} \sqrt{n_i^2 + n_s^2 - 2n_i n_s \cos\theta}, \qquad (2)$$

where n_i and n_s are the two refractive indices of the crystal for the directions of incidence and scattering. Since n_i and n_s can each take two values, there should be four pairs of values for (n_i, n_s) in equation (2). Further, for a given direction of elastic wave normal there are three types of elastic waves, each of which has a different velocity v_e. Thus from equation (2) it is easily seen that there are 12 possible values for $\Delta\nu$. In the case of a cubic crystal, the general equation (2) reduces to equation (1).

Although the existence of Doppler components in the light scattered by crystals was predicted by the theory of Brillouin as early as 1922, an experimental confirmation of the same was not forthcoming till much later. This is essentially due to the difficulties that beset an experimental observation of such low frequency shifts in the light diffused by crystals. In most of the crystals the frequency shifts of the Doppler components is of the order of ·5 to 3 cm.$^{-1}$ and consequently it is imperative to employ some high resolving power instrument to separate these. Besides, it is not often possible to procure large transparent crystals free from inclusions and the parasitic illumination which arise from these leads to the presence of the unmodified radiation along with the Brillouin components. Nevertheless, the fine structure of the scattered radiation predicted by theory was first observed by Gross (1930) in quartz and later by Raman and Venkateswaran (1938) in gypsum and L. Sibaiya (1938) in Rochelle salt. More recently the utilisation of the λ 2537 radiations of a quartz mercury arc in conjunction with a three metre quartz spectrograph by R. S. Krishnan (1947) and by Krishnan and Chandrasekharan (1950, 1951) has made possible an unambiguous recording and observation of these Brillouin components in quartz, diamond, alumina and a few other crystals and the existence of these in the light diffused by crystals may now be taken to be a well established fact.

It is now possible for us to make such an accurate study of the frequency shift, intensity and polarisation of these Doppler components that we will proceed to examine in detail the implications of the theory of thermal scattering of light in crystals. From equations (1) and (2) one finds that the frequency shifts $\Delta\nu$ of the scattered light are directly related to the elastic wave velocities. By a precise measurement of the frequency shifts of the Doppler components for different orientations of the crystal one can calculate

the acoustic velocities for different directions. From a knowledge of the effective wave vectors and using Christoffel's equation, one can now readily evaluate the elastic constants. Thus the thermal scattering of light in crystals and solids affords a new method for the determination of elastic constants.

2. Experimental Method

From what was said earlier, it will be evident that use of the visible radiations of the mercury arc makes it essential to employ large specimens free from incursions, etc., in order to record the genuine scattered radiation. This is particularly important since in most crystals, irregularities of a permanent nature like dislocations, etc., lead invariably to a certain amount of unmodified radiation in the nature of Tyndall scattering and this tends to a masking of the Brillouin components that are closeby. It is not always possible to have crystals which are free from such defects and satisfy the needs of the experiment. But these difficulties are easily obviated by the use of the resonance radiation of mercury for exciting the Brillouin components since the unmodified radiation can easily be eliminated from the scattered radiation by the use of a mercury vapour filter. Further as the intensity is proportional to λ^{-4} and n^8 the enormously increased scattering power in the ultraviolet is of added advantage and shortens the exposures necessary for recording the spectra. Over and above these advantages, the separation of the Brillouin components increases with the frequency of the incident radiation. The use of the resonance radiation therefore combined with Hilger three metre quartz spectrograph which has a dispersion of about 14 cm.$^{-1}$ in the λ 2537 region is adequate to make accurate measurements of the frequency shifts and to evaluate the elastic constants.

Using this technique, various crystals have been investigated in our laboratory and the results obtained therefrom are given in the next section.

3. Results and Discussion

In Plate X are reproduced the Brillouin spectra recorded with some typical crystals. In general it is found that except in the case of diamond the calcite, the transverse components are relatively weak in conformity with the theoretical calculations (V. Chandrasekharan, 1952, 1953). A quantitative verification of the directional variation of the acoustic wave velocity has been carried out so far only in the case of diamond and quartz. In Plate XI are reproduced the enlarged photographs of the spectra taken for four different orientations of a specimen of quartz with reference to the directions of incidence and observation. The first letter on the right-hand side of each photograph represents the direction of incidence while the

TABLE I

Cubic Crystals

No.	Crystal	Light incident along	Light scattered along	Angle of scattering in degrees	Direction of Elastic wave-normal	Nature of Brillouin components	Shift observed in $cm.^{-1}$	Effective elastic constant		
								Theoretical expression	Value calculated from observed shifts $\times 10^{-11}$ dynes/$cm.^2$	Value calculated from known elastic constants $\times 10^{-11}$ dynes/$cm.^2$
1	LiF	[100]	[010]	90	$[1\bar{1}0]$	Longitudinal	1·83	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	12·55	12·43
2	NaCl	[100]	[010]	90	$[1\bar{1}0]$	Longitudinal	1·44	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	4·80	4·31
3	KCl	[100]	[010]	90	$[1\bar{1}0]$	Longitudinal	1·21	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	3·34	2·93
4	Diamond	[111]	$[\bar{1}\bar{1}1]$	180	[111]	Transverse	7·0	$\frac{1}{3}(c_{11}+c_{12}+c_{44})$	36	33
		[111]	$[01\bar{1}]$	90	$\approx [4\bar{1},10]$	Longitudinal	8·7	..	112	105
		[111]	$[01\bar{1}]$	90	$\approx [4\bar{1},10]$	Transverse	5·59	..	46	38·7
		$[2\bar{1}\bar{1}]$	[111]	90	$\approx [\bar{1}44]$	Longitudinal	8·56	..	108	110·9
		$[2\bar{1}\bar{1}]$	[111]	90	$\approx [\bar{1}44]$	Transverse	5·63	..	47	41·7
		$[2\bar{1}\bar{1}]$	$[\bar{1}\bar{1}1]$	90	$\approx [811]$	Longitudinal	8·09	..	97	97·1
		$[2\bar{1}\bar{1}]$	$[\bar{1}\bar{1}1]$	90	$\approx [811]$	Transverse	5·88	..	51	42·6
		$[2\bar{1}\bar{1}]$	$[01\bar{1}]$	90	$\approx [3\bar{4}1]$	Longitudinal	8·50	..	107	111
		$[2\bar{1}\bar{1}]$	$[01\bar{1}]$	90	$\approx [3\bar{4}1]$	Transverse	5·58	..	36	37·3

TABLE II

Birefringent Crystals

No.	Crystal	Light incident along	Light scattered along	Angle of scattering in degrees	Direction of elastic wave-normal	Natufe of Brillouin components	Shift observed in cm.$^{-1}$	Effective elastic constant		
								Theoretical expression	Value calculated from observed shifts $\times 10^{-11}$ dynes/cm.^{2}	Value calculated from known elastic constants $\times 10^{-11}$ dynes/cm.^{2}
1	α-Quartz	[0$\bar{1}$0]	[001]	90	[011]	Longitudinal	1·90	..	10·80	9·83
	,,	[010]	[001]	90	[01$\bar{1}$]	Longitudinal	2·07	..	12·82	12·91
	,,	[100]	[001]	90	[101]	Longitudinal	1·96	..	11·23	11·69
	,,	[100]	[010]	90	[110]	Longitudinal	1·75	..	9·16	9·02
	,,	[100]	[$\bar{1}$00]	180	[100]	Longitudinal	2·36	c_{11}	8·33	8·54
	,,	[010]	[0$\bar{1}$0]	180	[010]	Longitudinal	2·22	$\frac{1}{2}(c_{11}+c_{44})$ $+\sqrt{\frac{1}{4}(c_{11}-c_{44})^2+c_{14}^2}$	7·37	9·32
	,,	[001]	[00$\bar{1}$]	180	[001]	Longitudinal	2·51	c_{33}	9·42	10·57
2	Calcite	[011]	[0$\bar{1}\bar{1}$]	180	[011]	Longitudinal	3·18	..	12·71	13·76
	,,	[011]	[0$\bar{1}\bar{1}$]	180	[011]	Longitudinal	2·89	..	12·22	13·76
	,,	[011]	[0$\bar{1}\bar{1}$]	180	[011]	Transverse	1·15	..	1·66	2·58
	,,	[011]	[0$\bar{1}\bar{1}$]	180	[011]	Transverse	1·41	..	2·90	2·58
3	Alumina	..	..	90	[001]	Longitudinal	2·45	c_{33}	21·4	56·3
4	Barite	[110]	[1$\bar{1}$0]	90	[100]	Longitudinal	1·55	c_{11}	10·84	8·83
	,,	[110]	[$\bar{1}$10]	90	[010]	Longitudinal	1·47	c_{22}	9·74	7·81
	,,	[001]	[00$\bar{1}$]	180	[001]	Longitudinal	2·13	c_{33}	10·23	10·38

second stands for the direction of observation (Fig. *a*) in Plate XI is the mercury spectrum heavily exposed in order to record the unabsorbed part of λ 2536·5 and its wings. In this picture, λ 2534·8 appears very broad due to overexposure. In accordance with the theoretical predictions, we notice a marked variation of $\Delta\nu$ with the orientation of the crystal with reference to the directions of incidence and scattering.

The measured values of the frequency shift of the Brillouin components observed in the case of four cubic crystals and four birefringent crystals are entered in Tables I and II. The directions of incidence, scattering and elastic wave normal with reference to the crystallographic axes of the specimens have also been given in the same tables. Using formulæ (1) and (2) given earlier, the values of the effective elastic constants have been calculated in all these cases and given in the last column (9) of Tables I and II. The last column of the same tables contains the corresponding values calculated from the known elastic constants using the theoretical expression given in Column 8. In some cases the theoretical expressions for the effective elastic constants are not given as they are very complicated. A critical study of Tables I and II reveals a fairly good agreement between the values of the effective elastic constants calculated from the observed Brillouin shifts and the corresponding values calculated from the elastic constants determined in the usual way. The only serious discrepancy noticed in the tables is in the case of alumina. This is due to the fact that the width of each component was nearly three-fourth of the observed shift (Krishnan, 1947). In all probability the observed width is due to the overlapping of the longitudinal and transverse components.

From an analysis of the results given above it is evident that accurate measurements of the shifts of Doppler components appearing in light scattered by crystals afford a new method for the determination of the elastic constants. Employing proper experimental technique, with specifically chosen directions of incidence and observation in the crystal and utilising in addition the polarisation characteristics of the different species, it is possible to separate unambiguously the Brillouin components due to the different acoustic waves and thereby investigate the complete elastic behaviour of crystals. In view of the sharp nature of the Brillouin components the accuracy attainable in the determination of the elastic constants by such light scattering studies is high.

4. SUMMARY

Details of the methods of evaluating the elastic constants of any crystal from the observed frequency shifts of the Brillouin components arising from

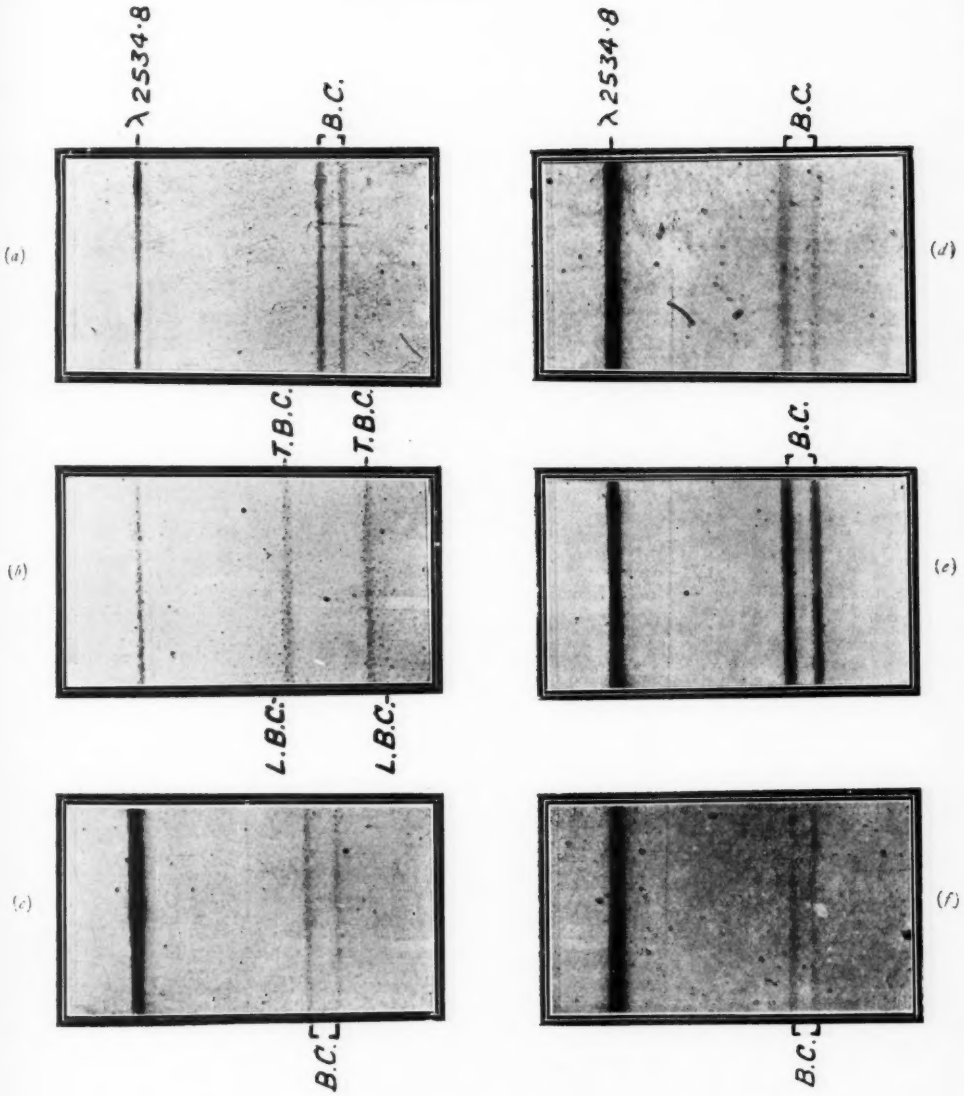

FIG. 1. The Brillouin spectra of crystals under ultra-violet excitation.

(*a*) Rock salt (*b*) Diamond (*c*) Barite
(*d*) Calcite (*e*) Quartz (*f*) Gypsum

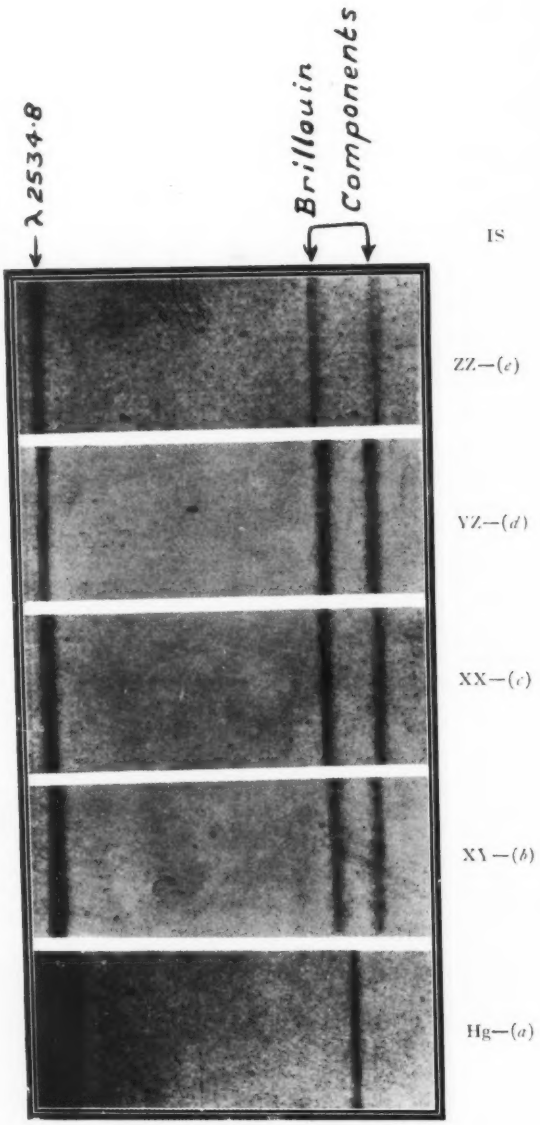

FIG. 2. (*a*). Heavily exposed mercury spectrum.
(*b*), (*c*), (*d*) & (*e*). Scattered spectrum of Quartz for four different orientations.

the thermal scattering of light have been indicated. From the measurements of the frequency shifts of the Brillouin components recorded using ultraviolet excitation in the case of four cubic crystals and four birefringent crystals, the effective elastic constants have been evaluated and have been compared with the values calculated using the elastic constants determined by other methods. The agreement is found to be very satisfactory. Thus light scattering in crystals affords yet another method of determining the elastic constants.

5. References

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THE THEORY OF THE ELASTICITY OF CRYSTALS

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I. Introduction

The subject of the elasticity of crystals has from its very early stages of development been approached from two distinct view-points which have resulted respectively in the phenomenological and the atomistic theories. The phenomenological theory was initiated by Green and Kelvin, and is founded on the continuum hypothesis of matter in solids. It is further built on the basis that the total energy of the solid is obtainable as the sum of the energies of the individual volume elements into which it can be subdivided. Each such volume element is supposed to possess a uniform density and the forces acting on it are assumed to be conservative, being derivable from a potential function. These remarks concerning the hypotheses underlying the phenomenological theory have been made here, in order to emphasize the limitations of the theory and to bring out the range of applicability of its results to any actual crystal composed of discrete atoms. It is obvious that these conditions can be incorporated for a crystal with a lattice structure only if the volume elements under consideration are large in comparison to the interatomic distances in the solid. The range of applicability of the phenomenological theory is therefore limited for crystals and its results can be expected to be sustainable only in relation to phenomena involving large volume elements, such as the propagation of non-dispersive waves of large wavelengths and low frequencies in the medium.

A fundamental problem of solid state physics is to interpret the macroscopic behaviour of crystals in terms of the constants characterising the lattice structure and the mutual interactions between pairs of atoms of the crystal. The importance of such an atomistic theory is mainly three-fold. Firstly, it enables us to examine the question whether the two theories would lead to identical results even in the range wherein the phenomenological theory is expected to be applicable. Secondly, it elucidates the nature of the vibrations in a crystal in regions that fall definitely outside the scope of the ordinary theory of elasticity, as in the case of dispersive waves in the medium. Finally, it holds out the hope of computing theoretically the

numerical values of the macroscopic constants. This is rendered possible because every crystal possesses a set of stationary normal modes of vibration whose frequencies are obtainable from spectroscopic data. The frequencies of these vibrations are also expressible in terms of the force-constants of the crystal. By a comparison of these two, the numerical values of at least a few of the force-constants can be ascertained and thus a possibility is opened up whereby the numerical values of the elastic constants become accessible to theoretical calculations as well.

The earliest attempt to provide an atomistic theory of elasticity is due to Cauchy. The investigations of Cauchy were however based on a somewhat outdated model of a solid, in which each atom is a centre of symmetry for the structure and the interatomic forces are strictly central. A direct consequence of these assumptions is that only fifteen among the twenty-one elastic constants emerging from Green's theory are independent, this reduction being effected by means of six relations that are generally known after Cauchy's name. Recent experiments have however proved that the Cauchy relations[2] are violated by a great number of crystals, even by most of the simplest variety of them, *viz.*, the cubic crystals. The failure of the Cauchy relations is clearly due to the assumption of central interactions among the atoms of the crystal, which might be true if each atom is simply an ion attracting the others in accordance with a law of force of the Coulomb type. But in any solid, the nucleii are all surrounded by clouds of electronic charges and any deformation of the substance would tend to change the energy of the electron cloud as well, thus producing forces that are non-central in character.

In order to be able to arrive at results that are in agreement with experimental data, it is therefore essential to start with a system of forces more general than a central force-scheme to represent the interatomic force-field inside crystals. An atomistic theory of elasticity based on such general system of forces was first provided by Begbie and Born[6, 7] and by Kun Huang.[5] By comparing the equations of long acoustic waves of low frequencies obtained from the atomistic theory with the equations of wave-propagation of the elasticity theory, these authors deduced expressions for the elastic constants of the crystal in terms of the force-constants. But the process of identification of the two sets of equations in their theories necessitated the assumption of a few relations among the force-constants which would be strictly true for central force systems only. Thus in spite of the formalism using a general force-scheme, the theories so far provided are reliable only for central interactions among the atoms of the crystal and do not adequately take account of the force-field existing inside crystals.

In this review, an attempt is made to present coherently the facts relating to the nature of the atomic vibrations inside crystals, and the general character of elastic deformations and wave-propagation inside crystals. A substantial part of the review is drawn from material contained in two papers already published by the author but it is made self-contained as far as possible. The contents of it are arranged in seven sections. Section one describes the notation adopted in the paper and introduces the basic concepts regarding wave-propagation in crystal structures. In Section II, we consider the state of movements of the atoms of the crystal arising from a disturbance confined initially to a small region of it. It is shown here that any arbitrary disturbance resolves itself into a superposition of the $(24\,p-3)$ harmonic vibrations predicted by the thoery of Sir C. V. Raman, and an elastic wave-motion that moves away from the region of the initial disturbance. In any region, the former modes are the only vibrations that possess significant amplitudes after a long time, and further these are independent of the conditions of the boundary of the crystal. Section III is devoted to a discussion of the long waves of low frequency inside the crystal, which are the analogue of the non-dispersive waves contemplated in the elasticity theory. Section IV concerns itself with the evaluation of the strain-energy function in the atomistic theory. An important fact emerging from this section is that the strain-energy function derived from the atomistic theory differs from the energy function of Green in that the former contains terms in the three rotational components of the strain also and thus involves forty-five independent elastic constants. A comparison of the two theories is possible only for the case of static strains which are strictly homogeneous or strictly irrotational. In these circumstances, expressions for the elastic constants as defined in the phenomenological theory can be obtained in terms of the atomic force-constants. Section VI deals again with wave-propagation inside crystals and it is shown here that except in the case of longitudinal waves, the equations of wave motion and the velocities of propagation of the elastic waves would be different in the two theories. Finally, the consequences of the forty-five constant theory as regards the stress-strain relations inside the crystal are discussed in Section VII.

I. PRELIMINARY CONCEPTS

We shall suppose that an unit cell of the crystal contains p atoms, and denote the three primitive translational vectors of the lattice by $\mathbf{d}_1$, $\mathbf{d}_2$ and $\mathbf{d}_3$. If the positions of the p atoms, which we can number as 1, 2, 3,....p, are all known inside any unit cell, then the structure of the crystal is completely specified. We denote by $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ the three primitive translational

vectors which generate the reciprocal lattice of the crystal. These are then determined from the relations

$$\mathbf{b}_i \cdot \mathbf{d}_j = \delta_{ij} \tag{1}$$

where δ_{ij} is the Kronecker delta symbol. Any vector $\mathbf{a}$ of the reciprocal lattice is therefore expressible as

$$\mathbf{a} = \theta_1\mathbf{b}_1 + \theta_2\mathbf{b}_2 + \theta_3\mathbf{b}_3 \tag{2}$$

Further, we use in the sequel the letters r and ρ as general symbols to represent any of the p atoms in the unit cell, and likewise denote by $\mathbf{s}$ and σ a general cell of the crystal lattice.

Taking any three mutually orthogonal axes x, y and z we represent the components of the displacements of the atom $(r, \mathbf{s})$ from its equilibrium position by q_{xrs}, q_{yrs} and q_{zrs}. If however the letters x or y occur under a summation sign in any expression, they should be understood as general summational indices that cover all the three directions of the co-ordinate axes of the system.

The expressions for the kinetic and potential energies of the crystal can now be written down. Denoting by $m_1, m_2, \ldots . m_p$ the masses of the p different atoms in the unit cell, we can write them as

$$2\mathrm{T} = \sum_{xrs} m_r \dot{q}^2_{xrs} \tag{3}$$

and

$$2\mathrm{V} = \sum_{xrs} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\ q_{xrs}\ q_{y\rho\sigma} \tag{4}$$

The equations of motion of the atoms of the crystal can be derived from (3) and (4) by means of a Lagrangian formulation. They are given by

$$-m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\ q_{y\rho\sigma} \tag{5}$$

The force-constants occurring in the above equations are not all entirely independent, but are connected to each other by means of a few relations which express the invariance conditions of the potential energy under pure translations. If the entire crystal is translated by an amount specified by the vector $\mathbf{u} = (u_x, u_y, u_z)$, then the left-hand side of the equation (5) should vanish and one therefore gets

$$\sum_{y\rho\sigma} u_y\ k^{y\rho\sigma}_{xrs} = 0 \tag{6}$$

As the vector **u** is arbitrary it follows that

$$\sum_{\rho\sigma} k^{\nu\rho\sigma}_{xrs} = 0 \ (x, y = \boldsymbol{x}, y, z) \tag{7}$$

Substituting the relations (7) in (5) we can rewrite the latter as

$$-m_r \ddot{q}_{xrs} = \sum_{\nu\rho\sigma} k^{\nu\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) \tag{5'}$$

The above equation expresses the fact that the total force acting in the x-direction on the atom $(r, \mathbf{s})$ is a linear sum of the forces due to the displacements of its neighbours, the force exerted by (ρ, σ) alone being equal to $-\sum_{\nu} k^{\nu\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs})$. The force-constant $k^{\nu\rho\sigma}_{xrs}$ can therefore be interpreted as the x-component of the force exerted by (ρ, σ) on the atom $(r, \mathbf{s})$ per unit relative displacement of these two atoms parallel to the y-direction.

Since the crystal is composed of p different homogeneous lattices, we shall suppose that a wave of given frequency and wave-length is propagated with different amplitudes inside the different Bravais lattices and that no damping of the waves occurs anywhere inside the crystal. The displacement of any atom caused by the propagation of a wave of frequency ν and wave-length λ travelling in the direction of the vector **e** through it is then expressible in the form

$$\mathbf{q}_{rs} = \mathbf{A}_r \, e^{2\pi i \left(\nu t - \frac{e.s}{\lambda}\right)} \qquad \text{or}$$

$$\mathbf{q}_{rs} = \mathbf{A}_r \, e^{i(\omega t - a.s)} \tag{8}$$

where

$$\omega = 2\pi\nu \text{ and } \mathbf{a} = \frac{2\pi}{\lambda} \mathbf{e}$$

By substituting these wave solutions in the equations of motions of the atoms of the crystal, we can now obtain a set of $3p$ linear equations in the $3p$ amplitudes $\mathrm{A}_r{}^x$, $\mathrm{A}_r{}^y$, $\mathrm{A}_r{}^z$ $(r = 1, 2, \ldots . p)$. A process of elimination of these amplitudes from these homogeneous equations then leads to the determinental equation

$$|\mathrm{A} - \mathrm{M}\omega^2)| = 0 \tag{9}$$

in which the elements of the matrix (A) composed of $3p$ rows and columns are the coefficients of the $3p$ amplitudes in the $3p$ sets of equations.

Equation (9) can also be rewritten in the form

$$s_0 \omega^{6p} + s_1 \omega^{6p-2} + \ldots . + s_{3p} = 0 \tag{9'}$$

The coefficients $s_1, s_2 \ldots . s_{3p}$ are functions of the wave vector **a**. The frequencies of the waves in the crystal are therefore dependent on their wavelengths, or the waves are dispersive. Further, there are $3p$ waves with a given wavelength, whose frequencies are the roots of (9) which correspond to this wave-vector.

II. Effect of an Arbitrary Disturbance

This section deals with the spreading of a disturbance, initially confined to a small region of the crystal, into its undisturbed portions at later instants of time. In view of the interaction among the atoms of the crystals, any local disturbance will gradually spread into the other regions of the lattice also, the rate of spreading depending on the strength of coupling between the various atoms of the crystal. To make the problem specific, we shall suppose that initially all the atoms in the cell (0, 0, 0) with index zero are displaced by small amounts and that the velocities of all other atoms are zero. In other words, the initial state of movements of the atoms is described by

$$\mathbf{q}_{rs}(0) = \frac{1}{8\pi^3 c} \int_{\Delta} \mathbf{u}_r \, e^{ia.s} \, dV = \mathbf{u}_r \, \delta_{so} \tag{10}$$

and

$$\dot{\mathbf{q}}_{rs}(0) = 0 \tag{11}$$

Here dV denotes the element of volume in the reciprocal space. If a_1, a_2, a_3 are the components of the wave vector in any three orthogonal directions and if c denotes the determinant of the transformation $a_i = \sum_j c_{ij}\theta_j (i, j = 1, 2, 3)$ where $\theta_1, \theta_2, \theta_3$ are the components of the wave vector along the directions of the axes of the primitive vectors of the reciprocal lattice, then $dV = da_1 \, da_2 \, da_3 = c \, d\theta_1 \, d\theta_2 \, d\theta_3$. Further Δ denotes the volume of the parallelopiped whose corners are given by $\pi \, (\pm \mathbf{b}_1 \pm \mathbf{b}_2 \pm \mathbf{b}_3)$.

The displacements of the atoms of the crystal from their equilibrium positions at a later instant can be determined by superposing waves of type (8) for all possible wavelengths and frequencies so that the final result reduces to the equations (10) and (11) for the case $t = 0$. If therefore we denote by $\omega_1^2, \omega_2^2, \ldots . \omega_{3p}^2$ the $3p$ different roots of (9) and their associated amplitudes by $\mathbf{A}_{r,1} \, \mathbf{A}_{r,2} \ldots . \mathbf{A}_{r,3p}$ $(r = 1, 2, \ldots . 3p)$, then by choosing the amplitude functions so as to satisfy the relation

$$\sum_{k=1}^{3p} \mathbf{A}_{r,k} = \mathbf{u}_r \tag{12}$$

we can represent the state of movements of the atoms of the crystal at any later instant by

$$q_{rs}(t) = \frac{1}{16\pi^3 c} \sum_{k=1}^{3p} \int_{\triangle} A_{r,k} \left(e^{i\omega_k t} + e^{-i\omega_k t} \right) e^{ia.s}\, dV \qquad (13)$$

A discussion of the above sum of $3p$ integrals for different values of t and s would reveal the nature of the disturbance at different instants and in the different regions of the crystal. We here consider only a simple and interesting case, namely the value of the above sum for large values of t.

This is done with the aid of the method of stationary phases introduced by Kelvin. The principle of Kelvin asserts that the value of an integral of the type

$$I = \int_{\triangle} f(\mathbf{x}) \exp i\{\omega(x)\, t - s \cdot x\}\, dV \qquad (14)$$

for large values of t arises only from the neighbourhood of points at which the function $\omega(x)$ is stationary. Such points are known as *saddle points.* We shall denote the stationary points of the function ω in the region of integration by $x_0, x_1 \ldots . x_i$. If the matrix whose elements are $a_{rs} = \left(\frac{\partial^2 w}{\partial x_r \partial x_s} \right)_{x=x_0}$ is denoted by $\triangle(x_0)$ and k denotes the difference between the number of positive eigenvalues of $\triangle(x_0)$ and the number of its negative eigenvalues, then the asymptotic value itself is given by

$$I \sim \left(\frac{2\pi}{t} \right)^{3/2} \sum_{x_0} \frac{f(x_0)}{|\triangle(x_0)|^{\frac{1}{2}}} \exp i\{\omega(x_0)\, t - s \cdot x_0 + k\pi/4\} \qquad (15)$$

the summation being over all the stationary points of the function ω inside the region of integration.

The above expression in fact denotes the first term in the asymptotic expansion of (14) in inverse powers of t and will represent integral (14) very closely if t is sufficiently large. It can be supposed to provide a fairly good estimate of (14) for all values of t greater than or equal to $K \mid s \mid^2$, where K is a constant of the dimensions of Time, for in this case $\omega(x)\, t$ is a quantity of second-order in largeness compared to the factor $\mathbf{s} \cdot \mathbf{x}$ occurring in the exponential of the integral.

The saddle points for the $3p$ integrals occurring in equation (13) are clearly the solution of the equations $\frac{d\omega_k}{da} = 0$ $(k = 1, 2 \ldots . 3p)$. In any

dispersive medium, the expression $\frac{d\omega}{da}$ represents the group velocity of the waves traversing it. Thus the saddle points correspond to waves for which the group velocity is identically equal to zero. It has now been shown elsewhere[10] that there are eight points in the reciprocal space for which the group velocities of waves traversing the crystal are equal to zero and for these, the components θ_1, θ_2 and θ_3 of the wave-vcctor $\mathbf{a}$ are all equal to either zero or π. Explicitly, these points are given by $\mathbf{a}^1 = (0, 0, 0)$; $\mathbf{a}^2 = (\pi, 0, 0)$; $\mathbf{a}^3 = (0, \pi, 0)$; $\mathbf{a}^4 = (0, 0, \pi)$; $\mathbf{a}^5 = (0, \pi, \pi)$; $\mathbf{a}^6 = (\pi, 0, \pi)$; $\mathbf{a}^7 = (\pi, \pi, 0)$; and $\mathbf{a}^8 = (\pi, \pi, \pi)$.

Considering first the vector $\mathbf{a}^1 = (0, 0, 0)$, it is readily observed from (8) that this corresponds to waves of infinite wave-length inside the lattice. It can be shown that for this case three of the roots of (9) vanish and that $\frac{d\omega_k}{da} \neq 0$ for these three frequency branches. Long waves associated with these three branches correspond to the elastic vibrations of the crystal and will be discussed later. For the remaining $(3p - 3)$ frequencies associated with this vector, as also for the $21p$ frequencies that are yielded by the seven other points listed above, the expression $\frac{d\omega_k}{da}$ vanishes. Thus we see that for a crystal containing p atoms in each of its unit cells, there are $(24p - 3)$ frequencies for which the group velocity of the waves vanishes.

Returning to the evaluation of (13) for large values of t, we note that the functions $\mathbf{A}_{r,k}$ and ω_k occurring in the $3p$ integrals are all periodic functions of the wave-vector $\mathbf{a}$ with periods equal to 2π for their components θ_1, θ_2 and θ_3 in the reciprocal lattice, and the region of integration of the integrals can therefore be slightly shifted about the origin without affecting their values so that it completely encloses all these eight saddle points. Then, denoting by $\triangle^\alpha k$, $\nu^\alpha k$ and $\mathbf{A}^\alpha_{r,k}$ the values of the functions $\triangle k$, ω_k and $\mathbf{A}_{r,k}$ at the eight saddle points, we can write the asymptotic value of the displacement of the atom $(r, \mathbf{s})$ as

$$\mathbf{q}_{rs}(t) = \frac{1}{c\,(2\pi t)^{3/2}} \sum_{k=4}^{3p} \frac{\mathbf{A}_{r,k}(1)}{|\triangle^1 k|^{\frac{1}{2}}} \cos(\nu^1 k\, t + k^1\pi/4)$$

$$+ \frac{1}{c\,(2\pi t)^{3/2}} \sum_{\alpha=2}^{8} \sum_{k=1}^{3p} \frac{\mathbf{A}_{r,\,k}^{(\alpha)}}{|\triangle k^\alpha|^{\frac{1}{2}}} \cos(\nu_k{}^\alpha t + \mathbf{a}^\alpha \cdot \mathbf{s} + k^\alpha\pi/4) \tag{16}$$

The above expression can be considered to give a good approximation of $q_{rs}(t)$ for all values of t greater than or equal to $K|s|^2$ where K is a constant characteristic of the medium having the dimensions of (Time).

Equation (16) suggests that in any region for which the above approximation is applicable, the vibrations of the atoms are all obtainable as a superposition of a set of harmonic vibrations which are characteristic of the crystal and hence may be appropriately called the characteristic vibrations of the crystal lattice. In the $(3p - 3)$ modes represented by the first sum, equivalent atoms in successive cells all vibrate with the same phase and amplitude. In the remaining $21p$ modes equivalent atoms in successive cells vibrate with the same amplitude but with opposite phases along one, two or three of the Bravais axes of the crystal, as each term in the second sum contains a factor $\cos \mathbf{a}^a . \mathbf{s}$ which is equal to *plus* or *minus* unity. Thus these modes are exactly identical with the stationary normal modes of vibration discussed in the dynamics of crystal lattices proposed by Sir C. V. Raman.[3-5] *Our theory therefore shows that the asymptotic nature of the vibrations of the atoms of the crystal arising from an arbitrary disturbance, confined initially to a small region of the lattice is a summation of the* $(24p - 3)$ *normal modes of vibrations recognised in Raman's theory.*

With the aid of the above results, it is possible to visualise at least qualitatively the nature of the vibration of the atoms at different instants of time and in different regions. In and very near the region of initial disturbance, the displacements of the atoms are representable by (16) even for small values of t and the disturbance therefore resolves itself into a superposition of the $(24p - 3)$ characteristic vibrations of the crystal almost immediately. In the farther off regions the disturbance spreads in the form of waves of which the fastest groups correspond to the elastic vibrations of the crystal. Since no atom can acquire a sensible amplitude until the fastest group reaches that lattice point, the maximum amplitude of any atom is attained only after a certain instant of time which depends on the velocity of propagation of the elastic waves in the medium. The value of the maximum amplitude can further be estimated to be of the order of t^{-1}, if we consider the elastic vibrations as surface waves divulging from a point whose energy is concentrated in a thin spherical shell only. The amplitudes of the atom thereafter fall away and for sufficiently large values of time comparable in magnitude with the square of the distance of any atom in a given region from the origin, the vibration of the atoms in this region consist of a superposition of the characteristic vibrations of the crystal with time-dependent amplitudes. At these instants, the elastic waves would have

completely moved away from the region under consideration, and their effects on the vibration of the atoms is therefore negligible, as can otherwise also be seen from the fact that the contributions of the elastic waves to the displacements of the atoms are infinitesimals of order higher than $t^{-3/2}$ and are therefore ignorable. Thus asymptotically in any region the characteristic modes of the crystal are the only vibrations that possess physically significant amplitudes, and the elastic waves which form a low frequency residue to them contribute none other than second order perturbation terms to the actual displacements of the atoms.

If the characteristic vibrations are assumed to settle in any region after an interval of time of the order r^2 where r is the distance of the region from the origin, then the rate of spreading of the disturbance $\frac{dr}{dt}$ at any point is inversely proportional to its distance from the centre. The vibrations therefore spread rapidly in the regions near the centre of disturbance but their rate of spreading diminishes for points in the farther off regions of the crystal. Another significant result that deserves mention is the dependence of the amplitudes of these vibrations on time, which indicates that these modes diffuse slowly into the volume of the crystal and do not travel outwards like elastic wave propagation in a medium. Further by the time these vibrations take to reach the external boundary of the crystal, their amplitudes would have become insignificant infinitesimals. Hence the characteristic vibrations are entirely uninfluenced by the boundary conditions of the crystal, and in discussing them all reference to its size and shape can be completely left out of account.

III. The Elastic Waves in the Crystal Lattice

We have already mentioned that three roots of equation (9) tend to zero in the limiting case of waves of infinite wave-length. Vibrations associated with these three roots of the secular equation (9) represent the elastic wave-motions inside the lattice and are propagated without any dispersion. For such vibrations, since $\underset{a\to 0}{\text{Lt}} \frac{\omega_k}{a} = \frac{d\omega_k}{da}$ the group and wave velocities become identical with the velocity of propagation of the elastic waves inside the crystal.

As in the classical elasticity theory, there can progress in any direction three types of elastic waves whose vibration directions are mutually orthogonal. Denoting by y and $\mathbf{e}$ the velocity and direction of propagation of sound waves, it can be shown[11] that the velocity of the three different waves

travelling in the direction of the unit vector **e** are given by the roots of the cubic equation

$$720\, a_0 y^3 + 360\, a_1 y^2 + 30\, a_2 y + a_3 = 0 \tag{17}$$

The coefficients a_0, a_1, a_2 and a_3 in the above equation are functions of the force-constants and are equal to the derivatives of s_{3p-3}, s_{3p-2}, s_{3p-1} and s_{3p} with respect to the variable a of orders 0, 2, 4 and 6 respectively. The velocities of the sound waves in crystals are therefore functions of the force-constants, which are the roots of the equation (17).

IV. THE DEFORMATION ENERGY FOR CRYSTALS

To obtain an expression for the deformation energy of the crystal, we first try to calculate the mutual energy between pairs of atoms of the crystal. The energy stored in any unit cell can then be obtained by summing up the mutual energy of interactions of the atoms in that cell with all the atoms of the crystal. We have already shown in Section I that the force exerted on the atom (r, s) in the x-direction by the displacement of the atom (ρ, σ) is equal to $-\sum_y k^{y\rho\sigma}_{xrs}(q_{y\rho\sigma} - q_{yrs})$. The mutual energy of this pair ($V^{\rho\sigma}_{rs}$) is obtained by multiplying the force by the relative displacement of the atoms, and dividing the result by two. Hence we have

$$V^{\rho\sigma}_{rs} = -\tfrac{1}{2} \sum_{xy} k^{y\rho\sigma}_{xrs}(q_{y\rho\sigma} - q_{yrs})(q_{x\rho\sigma} - q_{xrs}) \tag{18}$$

If $\triangle$ denotes the volume of the unit cell, the deformation energy stored in the cell **s** is given by

$$\triangle U = \tfrac{1}{2} \sum_r \sum_{\rho\sigma} V^{\rho\sigma}_{rs}$$

or

$$-4 \triangle U = \sum_{xr} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}(q_{y\rho\sigma} - q_{yrs})(q_{x\rho\sigma} - q_{xrs}) \tag{19}$$

Now each atom of the crystal should be in equilibrium in the deformed state also and hence one gets

$$\sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, q_{y\rho\sigma} = 0 \tag{20}$$

With the aid of (20) we can rewrite (19) also in the form

$$-4\triangle U = \sum_{xr} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, q_{x\rho\sigma}\, q_{y\rho\sigma} \tag{21}$$

Any deformation of the crystal can be analysed into two parts: a part which denotes the mutual displacements with respect to each other of the p

interpenetrating Bravais lattices and which is thus the same for all the atoms in the same lattice of the crystal; and another part which corresponds to the usual elastic deformations, denoting the continuous change in the relative displacements of the points of the body due to the strain. The former are generally known as the *inner displacements*.

Denoting now by k_{xr}, k_{yr}, k_{zr} the components of the inner displacements of the rth lattice, by x_{rs}, y_{rs}, z_{rs} the co-ordinates of the atom (r, s) in the underformed state and by u_{xy} $\left(= \frac{\partial u_x}{\partial_y}\right)$ the components of the strain, we can represent displacement components of the atoms due to the deformation by

$$q_{xrs} = k_{xr} + \sum_{\bar{x}} u_{x\bar{x}}\, \bar{x}_{rs} \tag{22}$$

Substituting (22) in (21) we can rewrite the energy expression as

$$-2U = \sum_{x\rho} \sum_{y\bar{y}} \left\{ {\rho \atop x y \bar{y}} \right\} k_{x\rho}\, u_{y\bar{y}} + \sum_{x\bar{x}} \sum_{y\bar{y}} [x\bar{x},\, y\bar{y}]\; u_{x\bar{x}}\, u_{y\bar{y}} \tag{23}$$

where

$$\left\{ {\rho \atop x y \bar{y}} \right\} = \frac{1}{\triangle} \sum_{r\sigma} k^{y\rho\sigma}_{xrs}\, \bar{y}_{\rho\sigma}$$

and

$$[x\bar{x},\, y\bar{y}] = \frac{1}{2\triangle} \sum_{r\rho\sigma} k^{y\rho\sigma}_{xrs}\, \bar{x}_{\rho\sigma}\, \bar{y}_{\rho\sigma} \tag{24}$$

The inner displacements can now be eliminated from the energy expression which can thus be expressed as a function of the strain variables only. The equations determining them are obtained by substituting (22) in (20) and are given by

$$\sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, k_{y\rho} = -\sum_{y\bar{y}} u_{y\bar{y}} \left(\sum_{\rho\sigma} k^{y\rho\sigma}_{xrs}\, \bar{y}_{\rho\sigma} \right) \tag{25}$$

These are a set of $3p$ equations in the $3p$ unknowns $k_{y\rho}$, etc., of which only $(3p - 3)$ can be linearly independent since the matrix multiplying them in the left-hand side is singular and is of rank $(3p - 3)$. Assuming that these equations are consistent and solvable and denoting by Γ the matrix that would multiply the column vector on the right-hand side in the solution of these equations, we can find the expressions for the inner displacements as

$$k_{xr} = -\sum_{y\rho} \sum_{s'y'} \sum_{\rho'\sigma'} u_{x'y'}\, \Gamma^{y\rho}_{sr}\; k^{s'\rho'\sigma'}_{yps}\; y'_{\rho'\sigma'} \tag{26}$$

Substituting (26) in (23) one gets

$$2U = \sum_{x\bar{x}} \sum_{y\bar{y}} d_{x\bar{x},\, y\bar{y}}\; u_{x\bar{x}}\, u_{y\bar{y}} \tag{27}$$

where

$$d_{x\bar{x},\, y\bar{y}} = -\,[x\bar{x},\; y\bar{y}] + (x\bar{x},\; y\bar{y}) \tag{28}$$

with

$$(x\bar{x},\; y\bar{y}) = \frac{1}{\triangle} \sum_{s'\rho} \sum_{r\sigma} \sum_{s'\rho'} \sum_{\rho_1\sigma_1} k^{s\rho\sigma}_{s'r\bar{s}}\, \bar{y}_{\rho\sigma}\, \Gamma^{s'\rho'}_{s'\rho}\, k^{\bar{s}\rho_1\sigma_1}_{s'\rho'\bar{s}}\, \bar{x}\rho_1\sigma_1 \tag{29}$$

Equation (27) gives the energy expression in the atomistic theory, and the constants multiplying the various quadratic terms in it are functions of the force-constants and the lattice parameters. We note that both the bracket expressions in (28) are symmetric in the pairs $x\bar{x}$, $y\bar{y}$. The round brackets are further invariant under a permutation of the symbols x and $\bar{x}$, or of y and $\bar{y}$, while the square brackets do not possess such a symmetry except in the special case of a central force system.

V. The Elastic Constants of Crystals[12]

If we write $e_{x\bar{x}} = (u_{x\bar{x}} + u_{\bar{x}x})$ for $\bar{x} \neq x$ and $e_{xx} = u_{xx}$ then the deformation energy obtained from the elasticity theory is a general quadratic in the six strain components e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{zx} and e_{xy}. Using the notation of Voigt in which the numbers (1, 2, 3, 4, 5, 6) replace respectively the symbols (xx, yy, zz, yz, zx, xy) the strain energy function of the elasticity theory can be written in either of these two forms

$$2U = \sum_{r,s}^{6} c_{rs}\; e_r\; e_s \tag{30}$$

$$= \sum_{x\bar{x}} \sum_{y\bar{y}} c_{x\bar{x},\, y\bar{y}}\; u_{x\bar{x}}\; u_{y\bar{y}}$$

The second form of the energy expression contains forty-five terms and the constants $c_{x\bar{x},\, y\bar{y}}$ are therefore subjected to the symmetry relations

$$c_{x\bar{x},\, y\bar{y}} = c_{x\bar{x},\, \bar{y}y} = c_{\bar{x}x,\, y\bar{y}} = c_{\bar{x}x,\, \bar{y}y} \tag{31}$$

so that it might become identical with the first one.

The expression (27) for the energy expression obtained from the atomistic theory can also be written in the form (30) provided the constants $d_{x\bar{x},\, y\bar{y}}$ also satisfy the same symmetry laws as the elastic constants, *i.e.*, if they are invariant under a permutation of the letters x and $\bar{x}$ or y and $\bar{y}$. But this is by no means the case, for these constants are functions of the force-

constants defined in accordance with the relations (24) and (29), and any assumption of such symmetry requirements can be shown to be equivalent to the assumption of a central force scheme for the interactions among the atoms of the crystal. As a central force interaction is not obeyed by a number of crystals, there is no justification whatsoever to suppose that these constants are also governed by relations (31) with the c's replaced by the d's.

The atomistic theory thus involves 45 independent constants for the case of a general strain* as had been stressed recently by Laval[9] and the present writer.[10] In order to derive expressions for the elastic constants in terms of the force-constants, it is therefore necessary to investigate the circumstances or conditions of strains under which expression (27) might reduce to the same mathematical form as that of (30) and which might thus enable us to identify the two. Obviously both these expressions reduce to the same form if

$$u_{xy} = u_{yx} \tag{32}$$

The above relation is clearly satisfied by irrotational strains. There is another type of strain which is important from the experimental standpoint, and which conforms to the above condition. These are the infinitesmal homogeneous deformations for which all the nine strain components are constants throughout the volume of the crystal. Any small homogeneous strain can now be analysed into a pure strain followed by a rotation about a suitable axis. By a proper choice of the co-ordinate axes it is always possible to make the rotational part of the strain vanish, and thus the relation (32) holds good for homogeneous strains also. By substituting (32) in (27) and comparing it with (30) we can now obtain expressions for the elastic constants determined by static homogeneous strains in terms of the force-constants, and they are given by

$$c_{x\bar{x},\, y\bar{y}} = \tfrac{1}{4}\left[d_{x\bar{x},\, y\bar{y}} + d_{\bar{x}x,\, y\bar{y}} + d_{\bar{x}x,\, \bar{y}y} + d_{x\bar{x},\, \bar{y}y}\right] \tag{33}$$

The constants appearing on the right-hand side of the above equation reduce to a fewer number than forty-five for crystals possessing symmetry. We shall consider the explicit relations following from (33) for crystals possessing the symmetry of the cubic class. If, as before, we introduce the convention of replacing the letter pairs (xx, yy, zz, yz, zy, zx, xz, xy, yx)

* Cases in which the energy function is a quadratic expression in the nine strain components have been considered in the phenomenological theory also, as can be inferred from a reference to a paper by Macdonald (*London Math. Soc. Proc.*, 1900, **32**, 311) given in Chapter VII of Love's book. Since this paper is not available to the author, it has not been possible to discuss the results contained therein in this article.

wherever they occur into the numbers (1, 2, 3, 4, 5, 6, 7, 8, 9), it can be shown that there are only four independent constants d_{11}, d_{12}, d_{44} and d_{45} for cubic crystals. The relations (33) reduce in this case to

$$\begin{aligned} c_{11} &= d_{11}; \\ c_{12} &= d_{12}; \\ c_{44} &= \tfrac{1}{2}(d_{44} + d_{45}) \end{aligned} \tag{34}$$

VI. WAVE-PROPAGATION INSIDE CRYSTALS

In this section we consider the nature of wave-propagation inside the crystal assuming that the strain produced by the propagation of a wave-front inside the crystal is very general and that the energy of the wave motion involves all the nine components of strain being given by the function (27). We shall assume all the nine strain components $u_{xy} = \dfrac{\partial u_x}{\partial y}$ are linearly independent functions of variables x, y and z. Then the equations of motions of the various elements of the crystal can be derived from the variational principle

$$\delta \int (\mathrm{T} - \mathrm{U})\, dt + \int \delta \mathrm{W}\, dt = 0 \tag{35}$$

in which U stands for the potential energy function (27) and T and W denote respectively the total kinetic energy of the solid and the work done by the external forces on the solid.

In the absence of body forces, W is given by

$$\delta \mathrm{W} = \sum_{x} \int (\mathrm{T}_{x\nu}\, \delta u_x)\, d\mathrm{S} \tag{36}$$

if $\mathrm{T}_{x\nu}$ denotes the normal component of the surface traction of the body, and the kinetic energy T is given by the expression

$$\mathrm{T} = \int \rho\, (\dot{u}_x{}^2 + \dot{u}_y{}^2 + \dot{u}_z{}^2)\, d\mathrm{V} \tag{37}$$

where ρ is the density of the medium.

The variational equations of (35) can now be written down and they are given by

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \sum_{\bar{x}} \frac{\partial}{\partial \bar{x}} \left(\frac{\partial \mathrm{U}}{\partial u_{x\bar{x}}} \right) \qquad (x \to x,\ y,\ z) \tag{38}$$

for interior points of the solid, and

$$T_{xv} = \sum_{y} \frac{\partial U}{\partial u_{xy}} \cos(y, \nu) \tag{39}$$

for points on the surface of the crystal.

We now seek to find out solutions of the above equations which are in the form of plane waves of the type

$$u_x = A^x \exp. \frac{2\pi i}{\lambda}(vt - e.r) \qquad (x \to x, y, z) \tag{40}$$

Substituting (40) in (38) one gets

$$\rho v^2 A^x = \sum_{x} \sum_{y\bar{y}} d_{x\bar{x}, y\bar{y}}\, e_{\bar{x}}\, e_{\bar{y}}\, A^y \qquad (x \to x, y, z) \tag{41}$$

If we write $A = (A^x, A^y, A^z)$ and $D_{xy} = \sum_{\bar{x}\bar{y}} d_{x\bar{x}, y\bar{y}}\, e_{\bar{x}}\, e_{\bar{y}}$ then the above equations can be rewritten as $(D - \rho v^2)A = 0$. The matrix $D = (D_{xy})$ is symmetric and hence its eigenvalues are real. If they are distinct, the corresponding eigenvectors are mutually orthogonal. Thus there are three types of elastic waves progressing in any direction of the crystal. Their vibrations directions are mutually perpendicular to each other, but they may be obliquely inclined to their direction of propagation.

Equations (41) are the equations of wave-propagation inside a crystal lattice and were first deduced by Begbie and Born. They had subsequently been used by several authors to obtain expressions for the elastic constants in terms of the force-constants. The first set of expressions were given by Begbie and Born, who obtained the relations

$$c_{x\bar{x}, y\bar{y}} = d_{x\bar{x}, y\bar{y}} \tag{42}$$

This relation is clearly untenable in a general force-scheme, for it amounts to assuming a central force-scheme, and would lead to the Cauchy relations for crystals possessing a centre of symmetry. For such crystals, the round brackets vanish and therefore $d_{x\bar{x}, y\bar{y}} = -[x\bar{x}, y\bar{y}]$. If further the relation (42) is satisfied, then the suffixes x and y are interchangeable in the expression for $d_{xx, yy}$, and similarly x and y or z are interchangeable in $d_{xx, yz}$. Therefore it follows from (33) that

$$c_{12} = c_{66};\ c_{23} = c_{44};\ c_{31} = c_{55};$$

$$c_{14} = c_{56};\ c_{25} = c_{46};\ c_{45} = c_{36} \tag{43}$$

which are the Cauchy relations. Thus the expressions of Begbie and Born are true in a central force scheme only and are not valid for the case of a general force system. A second set of relations for the elastic constants were later obtained by Kun Huang whose method also consists in identifying the lattice wave equations with the wave equations of the elasticity theory. But such an identification could be done only with the aid of a few additional relations such as $[x\bar{x}, y\bar{y}] = [\bar{x}x, \bar{y}y]$ which were assumed in Kun Huang's theory, and these were interpreted as the conditions for the vanishing of the initial stresses in an infinite lattice. We may mention that there is no justification for the assumption of these relations in a general force scheme which would hold good for central interactions between the atoms only. The expressions of Kun Huang are also not reliable in a general force scheme and can be expected to hold good for the case of central force systems only.

The real difficulty or source of error in identifying the lattice wave equations with those of the elasticity theory lies in the fact that they owe their origin to different potential functions in the variational method of deriving them. The former are derived from a potential function that contains the rotational part of the strain as well thus involving 45 independent constants, whereas the latter are derived from an energy expression involving 21 constants only. These two are not in general mathematically equivalent and are therefore not identifiable. For those cases of wave-propagation in which longitudinal waves moving in a certain direction alone are excited, the energy of the solid due to the wave motion will not involve the three rotational components of the strain, and in such cases both the theories would lead to identical results. But in general the equations of wave-motion and hence velocities of propagation of the waves are different in the two theories that involve twenty-one and forty-five constants respectively.

VII. THE STRESS-STRAIN RELATIONS

A natural question that arises in a forty-five constant theory is as regards the nature of the stress-strain relations in the solid. Since the potential energy of deformation in this case is a function of the nine strain variables, one can form nine quantities $T_{xy} = \frac{\partial U}{\partial u_{xy}}$ obtained by differentiating the energy expression partially with respect to the strain variables u_{xy}. If these are called the stresses acting on the body, then a striking property of the forty-five constant theory is that the stress tensor *does not* satisfy the symmetry property

$$T_{xy} = T_{yx} \tag{44}$$

If the surface tractions are the only forces acting on any volume element of the body, the result $T_{xy} = T_{yx}$ holds good at every point inside an elastic body which is under a state of stress. This is easily shown by considering the equilibrium of any small cube of volume l^3 with its centre at the origin and edges parallel to the axes and equating the total angular momentum parallel to the three axes to zero. In order to reconcile ourselves to the circumstance in which the nine stresses do not form a symmetric tensor, we shall assume that each volume element is being acted upon by a couple which tends to rotate it relative to its neighbouring elements in the solid, in addition to the surface tractions acting on it. Denoting by lW_x, lW_y, lW_z the components of the moment of the couple parallel to the three co-ordinate axes, we can obtain the equilibrium conditions of this element by equating the total angular momentum of the system to zero. This leads to

$$(T_{yx} - T_{xy}) + W_z = 0 \tag{45}$$

We shall now write

$$e_{xy} = \tfrac{1}{2}(u_{xy} + u_{yz})$$

and

$$\omega_z = \omega_{xy} = -\omega_{yx} = \tfrac{1}{2}(u_{xy} - u_{yx}).$$

Then obviously

$$T_{xy} = \frac{\partial U}{\partial u_{xy}} = \frac{1}{2}\left(\frac{\partial U}{\partial e_{xy}} + \frac{\partial U}{d\omega_z}\right) \text{ and } T_{yx} = \frac{1}{2}\left(\frac{\partial U}{\partial e_{xy}} - \frac{\partial U}{\partial \omega_z}\right).$$

Hence

$$(T_{yx} - T_{xy}) + \frac{\partial U}{\partial \omega_z} = 0 \tag{46}$$

Comparing (45) and (46) we see that the quantities $\frac{\partial U}{\partial \omega_x}, \frac{\partial U}{\partial \omega_y}, \frac{\partial U}{\partial \omega_z}$ denote respectively the components of the couple W_x, W_y, W_z acting on any small element of unit volume in the body.

We have already shown in Section IV that the quantities d_{11}, d_{12} and $\frac{1}{2}(d_{44} + d_{45})$ denote respectively the three elastic constants of cubic crystals for static homogeneous strains. A physical interpretation of the four constants occurring in the general theory will therefore be complete if it is possible to give a meaning to the quantity $(d_{44} - d_{45})$ which is independent of the above three. It then follows as a consequence of (45) applied to the case of cubic crystal that the constant $2(d_{44} - d_{45})$ is equal to the ratio of the magnitude of the couple acting on any volume element of the crystal to the magnitude of the rotation suffered by it due to the strain.

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